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ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.

In a letter addressed to Prof. Dana, printed in the *American Journal of Science and Arts*, and in another which appeared in the "Berichte" of the German Chemical Society, I have given a preliminary statement of my results in the study of the complex inorganic acids. The present notice is simply a report of further progress, and, like those which have already appeared, is to be regarded as provisional and subject to correction. I had proceeded but a little way in my investigations when I found it absolutely necessary to make a thorough study of the alkaline tungstates, which, as every chemist knows, are very numerous and varied in constitution. As the general result of my own study of the salts themselves and of the work of Scheibler, Marignac, Lotz, Forcher, Laurent, Lefort and other chemists who preceded me, I have arrived at a new classification and arrangement, which may be briefly stated as follows: There are two series of alkaline tungstates, the normal and the metatungstic series. To the normal series belong the salts respectively represented by the following formulas, which may be regarded as typical:

$WO_3.Na_2O + 2$ aq.
$2WO_3.Na_2O + 6$ aq. (Lefort.)
$3WO_3.Na_2O + 4$ aq. "

To the metatungstic series belong the following:

$4WO_3.Na_2O + 10$ aq. (Scheibler.)
$6WO_3.2BaO + 12$ aq. "
$8WO_3.3(NH_4)_2O + 8$ aq. (Marignac.)
$10WO_3.4Na_2O + 23$ aq.
$12WO_3.5Na_2O + 28$ aq. (Laurent, Marignac.)
$14WO_3.6Na_2O + 42$ aq. (Marignac.)

It will be seen that I have doubled several of the formulas which are usually received, and that in this way all the alkaline tungstates, the compositions of which have been well ascertained, are brought into simple and natural relations.

The antiquated mode of writing the formulas which I have employed presents the composition of the different salts in a clear point of view for the sake of comparison, and will therefore I hope be excused. I believe that it will be found that the alkaline molybdates admit of a similar classification, only the salts which we should naturally assign to the normal series are much more numerous, unless we consider some of those which belong apparently to this series to be acid. It may also be a question whether tungstates belonging to the type $6WO_3.2R_2O$ exist, since, if we admit the existence of tri-salts like that of Lefort, $3WO_3.Na_2O + 4$ aq., we should have a case of isomerism. Besides the tungstates above referred to and assumed as types, I have repeatedly obtained a double salt of sodium, the analyses of which conform very closely to the formula,

$10WO_3.4Na_2O + 12WO_3.5Na_2O + 51$ aq.

This may be written $22WO_3.9Na_2O + 51$ aq, and the progress of science, which tends constantly to show that the structure of inorganic molecules is more complex than we formerly supposed, may possibly oblige us to again double the formulas of the alkaline tungstates and introduce the 22-atom salt as a special term.

My published results as regards the complex inorganic acids and their salts require correction in a few particulars. Thus I have no salt of phosphotungstic acid containing more than 6 atoms of base, the 7 and 8-atom salts proving to be either

mixtures or salts of other series. The slightly soluble ammonium salts which I have obtained are represented by the formulas:

$40WO_3.2P_2O_5.5(NH_4)_2O + 40$ aq.

$60WO_3.3P_2O_5.8(NH_4)_2O + 37$ aq.

$80WO_3.4P_2O_5.11(NH_4)_2O + 96$ aq.

I regard all these as double salts, and have prepared barium salts corresponding to the two first mentioned. For the acid I find the formula,

$20WO_3.P_2O_5.6H_2O + 38$ aq.

considering it provisionally as six-basic. Two very well defined alkaline salts have respectively the formulas,

$20WO_3.P_2O_5.2Na_2O.4H_2O + 18$ aq.

$20WO_3.P_2O_5.2K_2O.4H_2O + 12$ aq.

The ratio of 20 atoms of WO_3 to 1 of P_2O_5 is that which here represents the analyses, but I have some evidence of the existence of salts in which the ratio is 24 to 1 and 18 to 1. Thus the analyses of a sodium salt agree well with the formula,

$24WO_3.P_2O_5.Na_2O.5H_2O + 27$ aq.

Debray found the ratio of MoO_3 to P_2O_5 in one series of phospho-molybdates 20 to 1. Rammelsberg has much more recently found the ratio 22 to 1, and finally Finkener considers it to be 24 to 1. I am disposed to think that all three ratios exist among the phospho-tungstates, and that there may be three corresponding classes of phospho-molybdates. I shall discuss this question carefully in my paper. Meantime I may remark that all known methods of determining phosphoric oxide P_2O_5 in the phospho-tungstates give results which are usually a little too low, as may easily be proved by qualitative tests. In consequence of the very high atomic weight of WO_3 the determination of the P_2O_5 must be extremely accurate to permit of much use of the method of computed ratios in assigning correct formulas.

My expectations as regards the possibility of generalizing results just obtained have been fully realized. Thus I have obtained finely crystallized antimonio-tungstates, and also antimonio-molybdates of sodium, potassium and ammonium. The analyses of the corresponding manganese salts agree well with the formulas,

$6WO_3.3Sb_2O_5.4MnO + 0$ aq.

$6MoO_3.3Sb_2O_5.4MnO + 30$ aq.

but these must be regarded as provisional only. Quantitative separations of tungsten and molybdenum from arsenic, antimony, vanadium, &c., present wholly new problems in analytical chemistry, and I have spent much time in effecting their solution. In like manner I have obtained splendidly crystallized vanadio-tungstates and vanadio-molybdates of potassium, sodium and ammonium. These salts have a fine orange color and are readily soluble in water, crystallizing only from syrupy solutions. I have, to say the least, reason to believe in the existence of similar salts containing SnO_2, TiO_2, ZrO_2, Nb_2O_5 and Ta_2O_5, but in all these cases, as well as with the compounds of PtO_2, IrO_2, &c., the chief difficulty consists in obtaining saturated salts, that is, salts in which WO_3 or MoO_3 have taken up all the deutoxide or pentoxide necessary to form a saturated compound. Add to this analytical and other difficulties and the task becomes a very formidable one, for which much time, labor and patience will be necessary.

CAMBRIDGE, March 5th, 1879.

ON NITROGEN IODIDE.

BY J. W. MALLET.

The various researches upon the highly explosive black substance formed by the action of iodine upon ammonia have, as is well known, led to different views of its composition. That first put forward by Colin and Gay Lussac, namely that it is nitrogen tri-iodide, appeared to have been set aside by the experiments of Serullas,* Millon,† Bineau,‡ Gladstone,§ Playfair, and Bunsen,‖ all of whom found hydrogen to be a constituent,

* Ann. Ch. Phys. [2] 42; 200 (1829).
† Ann. Ch. Phys. [2] 69; 78 (1838).
‡ Ann. Ch. Phys. [2] 70; 270 (1838) and [3] 15; 71 (1845).
§ Chem. Soc. Q. Jour. 4; 34 (1851).
‖ Ann. Ch. Pharm. 84; 1 (1852).

but in varying amount, the formulæ NHI_2—NH_2I—$NH_3.NI_3$—and $NH_3.4NI_3$ having been assigned to the products obtained by somewhat different processes, until more recently Stahlschmidt* has revived the statement that under certain conditions at least the simple tri-iodide is formed.

One source of error in the analysis of this instable compound seems to have received insufficient attention from some of those who have examined it, and somewhat affects the conclusions drawn from the experiments of others. The substance, obtained as a black powder by the action of iodine on ammonia, decomposes gradually in contact with water, nitrogen gas being slowly evolved, iodine liberated, and iodic and hydriodic acids or ammonium salts formed. This decomposition takes place to no inconsiderable extent during the drying of the powder at ordinary temperature, and may be readily proved to have occurred by treating the dry residue with any of the solvents for iodine, as for instance alcohol, chloroform, or carbon di-sulphide, which at once form deeply coloured solutions. Hence the air-dried powder is really a mixture of the original substance or substances with various decomposition products, and so is unsuited for accurate analysis. On the other hand it might be doubted in regard to the analyses made of freshly prepared and still moist iodide, whether the results apply to a substance capable of being obtained in the dry state without decomposition.

Millon and Bineau, it is true, seem to have aimed at guarding against this difficulty by drying the material, side by side with solid potash, under a jar of gaseous ammonia. Bineau remarks that some of the gas is at first absorbed by the water moistening the powder, but that as the drying proceeds the gas recovers ("à peu près") its original volume, and that so moisture is gotten rid of without the iodide being decomposed. But, without qualitative examination of the gas, or a very accurate determination of its volume, this does not afford satisfactory proof that the dry substance is unchanged. I have observed continuous, though slow, evolution of little bubbles of nitrogen from the freshly prepared powder *when kept under strong aqueous ammonia*, though in this case no free iodine can be found, since as fast as it is liberated it reacts with the ex-

* Pogg. Ann. 119; 421 (1863).

cess of ammonia, reproducing the nitrogen iodide, and forming more ammonium iodide, which latter therefore tends to accumulate in the liquid, and is thus to be found in the residue from drying up a moist mass of the powder in an atmosphere of ammonia.

I have applied a different method, which is often useful under other circumstances, for quickly getting rid of water, namely, repeated and rapid washing with absolute alcohol, followed by ether, and final evaporation of the last-named volatile liquid.

20 or 30 grms. of iodine was dissolved in a minimum of 95 per cent. alcohol, and precipitated by pouring into a large volume of cold water. The finely divided iodine was washed several times by decantation, then gently triturated for several minutes in a porcelain mortar with a large excess of the strongest liquid ammonia kept at or below 0° C. by a freezing mixture, the liquid poured off from the easily subsiding black powder, and replaced two or three times by fresh solution of ammonia. The powder was then at once transferred to a corked flask, and shaken up repeatedly, first with alcohol of 95 per cent., then with absolute alcohol, and finally with anhydrous ether, all of these liquids being artificially cooled. Most of the last portion of ether, which, as well as several of the preceding washings, was perfectly colourless, having been decanted off, the fluid black mud was turned out upon a filter, drained in a few moments, and the remains of the ether swept away as vapour by placing the filter and contents under a receiver and drawing cold dry air through in a rapid stream. This use of alcohol and ether to remove water from the iodide after its formation is not to be confounded with the employment by several experimenters of alcoholic solutions of iodine or ammonia, or both, in *making* the substance in the first instance.

The product thus obtained was explosive in the highest degree, yielding to very slight friction upon paper, frequently producing a crackling sound from little partial explosions when it was gently rubbed under water, and in two instances exploding in some quantity under water, with much violence and complete shattering of the vessel.

The relative quantities of nitrogen and iodine were ascer-

tained by decomposing an unweighed parcel of the substance by a moderately strong aqueous solution of sodium sulphite, neutralized by dilute sodium hydrate, and determining, in equal volumes of the liquid, the nitrogen as ammonia (expelled by boiling with excess of soda, and collected in sulphuric acid of standard strength), and the iodine as silver iodide.

A—In three experiments were obtained,

	No. 1	No. 2	No. 3	
NH_3	.126	.184	.172	grm.
Equiv. to N	.104	.152	.142	"
Ag I	5.126	7.607	6.889	"
Equiv. to I	2.771	4.112	3.723	"

Nos. 1 and 2 refer to the same lot of material (separately decomposed, however); No. 3 to the product from a repetition of the same process.

These numbers correspond to,

	No. 1	No. 2	No. 3	Calc. for NI_3
N (assumed)	14.	14.	14.	14.
I	373.02	378.74	367.04	381.

or, for 1 atom of nitrogen,

	No. 1	No. 2	No. 3
Atoms of iodine	2.94	2.98	2.89

B—Another specimen, similarly prepared, but with weaker ammonia, without any precaution as to cooling the materials used, and in a room the temperature of which was about 23° C., gave

	No. 1	No. 2	
NH_3	.174	.152	grm.
Equiv. to N	.143	.125	"
Ag I	5.935	5.467	"
Equiv. to I	3.208	2.955	"

corresponding to,

	No. 1	No. 2
N (assumed)	14.	14.
I	314.07	330.96

or, for one atom of nitrogen,

	No. 1	No. 2
Atoms of iodine	2.47	2.61

C—Two other specimens, washed at first, not with alcohol and ether, but simply with water until no free ammonia could be detected in the washings, then kept under water for two or three days at ordinary temperature, with occasional stirring,

and finally dried after washing out with absolute alcohol and ether, as above described, gave

	No. 1	No. 2	
NH_3	.136	.127	grm.
Equiv. to N	.112	.105	"
Ag I	3.954	3.667	"
Equiv. to I	2.137	1.982	"

corresponding to,

	No. 1	No. 2
N (assumed)	14.	14.
I	267.12	264.27

or, for 1 atom of nitrogen,

	No. 1	No. 2
Atoms of iodine	2.10	2.08

Of the above results,

A distinctly represents the atomic ratio $N : I = 1 : 3$, fully confirming Stahlschmidt's conclusion that the tri-iodide can be obtained quite free from hydrogen.

B corresponds well with $N : I = 2 : 5$, and

C with the proportion found as the result of several earlier experiments, $N : I = 1 : 2$.

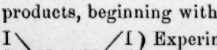
If B be admitted to stand for a definite compound, and not a mere mixture of A and C, which is rendered probable by the fairly close agreement of the results obtained with the calculated figures, there must be two atoms of nitrogen in the molecule, and the formula will be N_2HI_5. This formula may almost as well be deduced from Bunsen's analysis of one of the products he obtained (by addition of ammonia to a solution of iodine in nitro-hydrochloric acid, diluted with water, and rapidly washing with cold water) as that which he has himself assigned, viz. $NH_3.4NI_3$, since the figures stand

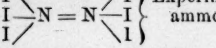
	Calc. for N_2HI_5.	Calc. for $NH_3.4NI_3$.	Found by Bunsen.
N	4.22	4.38 . . .	.008143 or, assumed 4.38
H	.15	.19 . . .	
I	95.63 . . .	95.43 . . .	.174417 93.82*
	100.	100.	

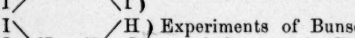
*There seems to be an error in the calculation of the percentage of iodine in the original paper (Ann. d. Ch. u. Pharm.; 84; 1), but the figures here given are correctly deduced, I believe, from the actual weighings quoted, viz. .1300 grm. of ammonio-chloride of platinum and .0732 grm. of palladium.

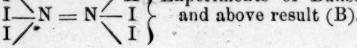
It will be seen that the figures of the formula now proposed differ less from those of Bunsen's formula than the latter do from the results of experiment.

In view of the general fact that the compounds of nitrogen in which this element behaves as a pentad are those in which instability is chiefly observable, and noticing the various proportions in which iodine and hydrogen have been found together united with it, it seems fairly probable that the molecule of each of these explosive compounds contains two pentad nitrogen atoms; and reviewing all that has been published on the subject, with attention to the sources of error connected with the various methods used, we seem to have established the existence of the following series of substituted products, beginning with the tri-iodide:

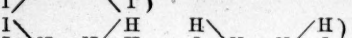

Experiments of Stahlschmidt (using aqueous ammonia), and those now reported (A).


Experiments of Bunsen (second product), and above result (B).


Experiments of Bineau, Stahlschmidt, Gladstone (using alcoholic solutions of ammonia and iodine), and above result (C).


Experiments of Bunsen (first product, using anhydrous alcoholic solutions of ammonia and iodine). He himself assigned the formula $NH_3.NI_3$.

It is much more doubtful whether we should add,


Experiments of Millon (in 1838). The product dried under a receiver filled with gaseous ammonia, had lost its extreme explosiveness, and no doubt contained ammonium iodide.

It appears that, not only may these different products be obtained by varying the conditions under which the formation of the explosive substance is effected, but during its decomposition by water, certainly involving more than a single series of reactions, one of these products may be more or less converted into others.

UNIVERSITY OF VIRGINIA, *Feb.* 21, 1879.

DISCUSSION OF THE WORKING HYPOTHESIS THAT THE SO-CALLED ELEMENTS ARE COMPOUND BODIES.*

By J. Norman Lockyer, F. R. S.

The author has been engaged for the last four years in preparing a map of the solar spectrum on a large scale, the work including a comparison of the Frauenhofer lines with those visible in the spectrum of the vapor of each of the metallic elements in the electric arc.

The first thing to be accomplished was the purification of the spectra, that is, the determination of which lines properly belonged to the spectrum of any given element and which ones were really due to impurities. When, for instance, an impurity of manganese was searched for in iron, if the longest line of manganese was absent the short lines must also be absent, on the hypothesis that the elements are elementary; if the longest line was present then the impurity was traced down to the shortest line present.

In the case of iron the final reduction showed coincidences between the short lines of the spectrum of this element and the short lines of a large number of other elements. Among these elements are vanadium, uranium, zirconium, yttrium, platinum, &c. In a table given in the original article it is shown that the line 3906 of the iron spectrum coincides with a line of uranium, yttrium and zirconium. There are also two other lines of uranium, viz. 3934 and 3954; two of yttrium, viz. 3947 and 3962; and one of zirconium, viz. 3965, all of which coincide with known short iron lines. So also in the case of titanium coincidences are noticed between the lines of this element and those of zirconium, manganese, cerium, didymium, &c.

The final reduction of the spectra of all the metallic elements in the region 39-40 showed that the hypothesis that identical lines in different spectra are due to impurities is not sufficient.

*Abstract of a paper read before the Royal Society, Dec. 12, 1878 (Amer. Jour. Sci., vol. xvii, p. 93).

For we find short-line coincidences between many metals the impurities of which have been eliminated, or in which the freedom from mutual impurity has been demonstrated by the absence of the longest lines.

The author had previously been led, through considerations in solar and stellar physics, to the hypothesis *that the elements themselves, or at all events some of them, are compound bodies;* and now as the old hypothesis that the elements are elementary led only to confusion, it was determined to try the application of the new one to the facts observed.

Obviously the first thing to be done was to inquire whether the hypothesis would explain these short-line coincidences. Calling, for sake of simplicity, the short lines common to many spectra *basic lines*, the new hypothesis, to be of any value, should present us with a state of things in which basic molecules representing bases of the so-called elements should give us their lines, varying in intensity from one condition to another, the *conditions* representing various compoundings.

Suppose A (nickel, let us say) to contain B (cobalt) as an impurity, and as an element, what will be the difference in the spectroscopic result?

A in both cases will have a spectrum of its own.

B as an impurity will add its lines according to the amount of impurity, as has been shown in previous papers.

B as an element will add its lines according to the amount of dissociation, as has also been shown.

The difference in the phenomena, therefore, will be that, with gradually increasing temperature, the spectrum of A *will fade*, if it be a compound body, as it will be increasingly dissociated, and it *will not* fade if it be a simple one.

Again, on the hypothesis that A is a compound body, that is, one compounded of at least two similar or dissimilar molecular groupings, then the longest lines at one temperature will not be the longest at another, the whole fabric of "impurity elimination," based upon the assumed single molecular grouping, falls to pieces, and the origin of the basic lines is at once evident.

Now to apply this reasoning to the dissociation of a known compound body into its elements.

A compound body, such as a salt of calcium, has as definite

a spectrum as a simple one; but while the spectrum of the metal itself consists of lines, the number and thickness of some of which increase with increased quantity, the spectrum of the compound consists in the main of channelled spaces and bands which increase in like manner.

In short, the molecules of a simple body and a compound one are affected in the same manner by quantity in so far as their spectra are concerned; *in other words, both spectra have their long and short lines*, the lines in the spectrum of the element being represented by bands or fluted lines in the spectrum of the compound; and in each case the greatest simplicity of the spectrum depends upon the smallest quantity, and the greatest complexity (a continuous spectrum) upon the greatest.

The heat required to act upon such a compound as a salt of calcium so as to render its spectrum visible, dissociates the compound according to its volatility; the number of true metallic lines which thus appear is a measure of the quantity of the metal resulting from the dissociation, and as the metal lines increase in number the compound bands thin out.

It has been shown in previous papers how we have been led to the conclusion that binary compounds have spectra of their own, and how this idea has been established by considerations having for a basis the observations of the long and short lines.

It is absolutely similar observations and similar reasoning which will be brought forward in discussing the compound nature of the chemical elements themselves.

The author now discusses certain phenomena observed in connection with the element calcium which show that the spectrum of this element undergoes changes under the influence of rising temperature, and that these changes are similar to those which the spectrum of a salt of calcium undergoes under similar conditions. As this case is fully considered in the following article,* it is unnecessary to take it up here.

The spectrum of iron may be described as a very complicated spectrum, so far as the number of lines is concerned, in comparison with such bodies as sodium and potassium, lead, thallium, and the like, but unlike them again it contains no one

* P. 15.

line which is clearly and unmistakably reversed on all occasions. Compared, however, with the spectrum of such bodies as cerium and uranium the spectrum is simplicity itself. Only a very small part of the spectrum is here considered, viz. the portion between H and G. Among the lines there are two triplets, two sets of three lines each; and the facts indicate that these two triplets are not due to the vibration of the same molecular grouping which gives rise to most of the other lines. The facts are as follows: In many photographs in which iron has been compared with other bodies, and in others again in which iron has been photographed as existing in different degrees of impurity in other bodies, these triplets have been seen almost alone, and the relative intensity of them, as compared with the few remaining lines, is greatly changed.

Further, in solar storms, as is well known, the iron lines sometimes make their appearance in the chromosphere. Now, if we were dealing here with one molecular grouping, we should expect the lines to make their appearance in the order of their lengths, and we should expect the shortest lines to occur less frequently than the longest ones. But precisely the opposite is the fact, as has been shown by Young in his observation of the chromospheric lines, made at Sherman, in the Rocky Mountains.

The question next arises, are the triplets produced by one molecular grouping or by two? The facts also help us to answer this question. It may be stated by way of reminder that in the spark photograph the more refrangible triplet is barely visible, while the one near G is very strong. Now, if one molecular grouping alone were in question this relative intensity would always be preserved, however much the absolute intensity of the compound system might vary; but if it is a question of two molecules, we might expect that in some of the regions open to our observations we should get evidence of cases in which the relative intensity is reversed or the two intensities are assimilated. What might happen does happen: the relative intensity of the two triplets in the spark photograph is grandly reversed in the spectrum of the sun. The lines barely visible in the spark photograph are among the most prominent in the solar spectrum, while the triplet which is strong in that photograph is represented by Frauenhofer

lines not half so thick. Indeed, while the hypothesis that the iron lines in the region referred to are produced by the vibration of one molecule does not include all the facts, the hypothesis that the vibrations are produced by at least three distinct molecules includes all the phenomena in a most satisfactory manner.

Changes in the lithium spectrum have also been observed by Frankland and Tyndall. It has been shown that a blue line occurs in this spectrum at high temperatures and that its intensity increases as the temperature rises. In a postscript to a letter written by Frankland to Tyndall in 1861, the following passage is found: "I have just made some further experiments on the lithium spectrum, and they conclusively prove that the appearance of the blue line depends entirely on the temperature. The spectrum of lithium chloride, ignited in a Bunsen's burner flame, does not disclose the faintest trace of the blue line; replace the Bunsen's burner by a jet of hydrogen (the temperature of which is higher than that of the Bunsen's burner) and the blue line appears, faint, it is true, but sharp and quite unmistakable. If oxygen now be slowly turned into the jet, the brilliancy of the blue line increases until the temperature of the flame rises high enough to fuse the platinum, and thus put an end to the experiment."

Taking up, finally, the case of hydrogen, the author remarks that all the phenomena of variability and inversion in the order of intensity presented to us in the case of calcium can be paralleled by reference to the knowledge already acquired regarding the spectrum of hydrogen. He and Frankland showed that the whole complicated spectrum of hydrogen can be reduced *to one line in the green*, corresponding to F in the solar spectrum. The observations made during eclipses have shown that at the time when the hydrogen lines were most brilliant in the corona, the calcium lines were not detected; next, when, the hydrogen lines being still brilliant, the *h* line was not present (a condition of things which, in all probability, indicated a reduction of temperature), calcium began to make itself unmistakably visible; and finally, when the hydrogen lines are absent, they become striking objects in the spectrum of the corona. In regard to the *h* line Frankland and the author showed in 1869 that it only made

its appearance when a high tension was employed. It was absent from among the hydrogen lines during the eclipse of 1875. And now this evidence is strengthened by the remark that it is always the shortest line of hydrogen in the chromosphere.

Assuming then that the spectra of the elements change in the manner described, under the influence of rising temperature, a perfect continuity of phenomena is established on the hypothesis of successive dissociations, analogous to those observed in the cases of undoubted compounds.

ON LOCKYER'S "HYPOTHESIS THAT THE SO-CALLED ELEMENTS ARE COMPOUND BODIES."*

By C. S. Hastings,

Assistant Professor of Physics, Johns Hopkins University.

This paper is a discussion of certain phenomena observed in the course of a long investigation of the solar spectrum and the spectra of the various elements. In the discussion, the writer is led to the conclusion that the facts observed are only reconcilable on the assumption that, at the highest attainable temperatures, the bodies known to the chemist as elementary are dissociated into other forms of matter less complex; and, as all elements are supposed to undergo this degradation at sufficiently high temperatures, the inference is, that the chemical elements themselves bear the same relation to some simpler form or forms of matter, that chemical compounds do to these elements.

The idea of such a relation is by no means new, but, as this is the first bit of experimental proof offered, it is of the

*Am. Jour. Sci. Vol. XVII. p. 93; see also preceding article.

highest interest. We shall here examine the nature of this evidence.

The argument is founded on two classes of phenomena :

1st. Numerous coincidences in lines of iron and of titanium with those of many other elements, the metals mentioned being assumed as spectroscopically pure.

2d. Analogies between the character of spectra of the same vapor under varying circumstances, and the spectra of vapors known to be compound.

Clearly the vulnerable point in the deduction from the first class of phenomena is the assumption that the iron, for example, is spectroscopically free from the impurity which would yield the lines in question. Before any weight can be attached to the argument, this assumption must be justified. Lockyer's proof of this essential purity is the absence of the "long" lines which are asserted to be characteristic of the spectrum of the impurity under all circumstances. To thoroughly understand the significance of this reasoning we must define the term long line.

If we examine spectroscopically a limited volume of incandescent vapor, not uniformly luminous in all parts, we shall find a certain number of lines in the most brilliant portion which grows progressively less as we approach the less brilliant portion. If the image of this vapor be projected upon the slit of the collimator, and of such a size as not to entirely cover it, certain lines will be traced nearer the limit of the duller portion than others. These are the longer lines. Practically we can secure these conditions best by means of the electrical discharge between terminals of the substance, the spectrum of which we wish to study. These lines are almost always the most brilliant in the spectrum, the first to appear and the last to disappear under any modification of the experiment. Are they long simply because they are the more intense? *i. e.* do the short lines disappear in decreasing the intensity of the light merely because they fall below the value necessary to stimulate the retina or impress the sensitive plate? or, on the other hand, is there besides this evident difference of degree a physical difference of kind? If the first, Lockyer's proof is complete; if the second, the proof is defective and with it the conclusion.

If we examine the spectrum of incandescent hydrogen, sufficiently brilliant, we see three or four lines, by far the most prominent being the line in the red corresponding to the C line of the solar spectrum, and that in the blue-green of the same refrangibility as the F line: of these two the C line is much the more conspicuous. If this advantage in favor of C be due to its greater subjective intensity, we know from Fechner's law that it will be more apparent with diminution of the intensity of the source. We may readily subject this conclusion to the test of experiment, either by observing the light after reflection from some white screen, such as paper or plaster, which exerts no selective absorption, or better, by throwing an image of the electric discharge through hydrogen on the slit of the collimator by a lens, the aperture of which may be reduced at will. Clearly, by neither of these processes do we modify the nature of our light; but by either process we find that the F line alone survives after considerable diminution and is consequently the brighter line. But, if the relative lengths of any two spectral lines are determined beyond cavil they are these very two. As hydrogen is the characteristic and ever-present element in the chromosphere, it has been studied from the time that the spectroscope was first applied to the examination of this phenomenon, and from that time it has been recognized that the C line is the longer. This experiment* then proves that an element may be present, giving a spectrum, but without its longest line. As a still more important deduction we see that a line may be "long," as defined above, from two different reasons; one, on account of greater intensity, the other a less evident cause which we shall discuss further on. As a matter of convenience we will style the former *persistent* lines and the latter the *long* lines proper. Evidently the *persistent* line does not always retain this property, but the long line, distinguished by a physical difference, is always long; *e. g.* F is the persistent line in our vacuum tube and probably at the base of the chromosphere; C is the persistent line higher up in the chromosphere and the long line everywhere. As Lockyer's method does not distin-

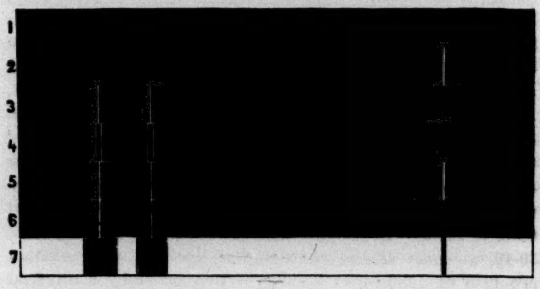
*The experiment is but a less objectionable form of proof of what Huggins announced long ago when studying the spectra of nebulae, though its significance seems to have been overlooked. The "certain conditions of temperature and pressure" of Frankland and Lockyer which give F alone are simply such as give sufficiently small intensity of light.

guish between these two kinds of lines, but practically eliminates impurities only until those which were the persistent lines, under the conditions governing his observations of the impurity in question, have disappeared, his conclusions are unwarrantable.

We shall see farther on other instances of the distinction explained above, not less clear.

There remains one point in what precedes worthy of a moment's explanation. The C line is recognized as the most conspicuous in the hydrogen spectrum, but is proved not the most brilliant. This is no contradiction. This line occupies a place in that portion of the spectrum which alone is nearly saturated; the F line on the contrary falls very near that region which, by virtue of the properties of the retina, appears least saturated, whereas the more refrangible portion is lowered in saturation by the fluorescence of the media of the eye.

Of the phenomena of the second class, the only set complete in itself and in the discussion of which the reasoning is succinct and consecutive, is that relating to calcium. The accompanying figure with its description, taken from Lockyer's



The blue end of the spectrum of calcium under different conditions. 1. Calcium is combined with chlorine ($CaCl_2$). When the temperature is low the compound molecule vibrates as a whole, the spectrum is at the red end and no lines of calcium are seen. 2. The line of the metal seen when the compound molecule is dissociated to a slight extent with an induced current. 3. The spectrum of metallic calcium in the electric arc with a small number of cells. 4. The same when the number of cells is increased. 5. The spectrum when a coil and small jar are employed. 6. The spectrum when a large coil and large jar are used. 7. The absorption of the calcium vapor in the sun.

paper, almost interprets itself. The author supposes up to 6 inclusive, that the only changes in appearance are due to change in temperature. Clearly, 2 is derived from 1 by a partial dissociation of the chloride, the former still exhibiting, it may be, the lines which were alone present in the latter. By analogy, Lockyer supposes 3 derived from 2 by partial dissociation of the element calcium. Here, doubtless, all the lines belonging to the chloride have disappeared, a result attained by simple increase of temperature. If the former reasoning is true we have only to increase our temperature until the element calcium is completely dissociated, when the line in 2 will vanish just as and for the same reason that the lines in 1 have vanished. This expectation we find justified in 6. Here we have, in our opinion, the strongest evidence which Lockyer has offered in favor of his hypothesis.

The phenomena, as far as discussed, are certainly explained by it, and in a simple manner. But let us see what points it leaves unexplained. In 3 we find one line reversed, the other two simple, while in 4 all are reversed. In 6 we find a temperature so high that the compound (calcium) cannot exist, but 7 asserts the existence of this compound in the sun, hence a lower temperature. That the temperature of the sun is below that of any artificial source is surprising, and was certainly heretofore thought improbable.

It is in the necessary deductions from this hypothesis, however, that we find its strongest objections. If the pair of lines to the left in the cut belong to a product of dissociation, then each one belongs to a different product, since they are separated occasionally in the chromosphere and always in the spectrum of Sirius. In the case of iron, even in the limited region 39-40, we must assume, according to Lockyer, three distinct products of dissociation. In hydrogen, by the same logical process we must, if we correctly apprehend the argument, assume not less than five products resulting from successive increase of temperature. Nor is there any indication that we are approaching an ultimate elementary form of matter which will put an end to indefinite complication, for none of these lines thus derived have the same refrangibility. But when we recognize that on this hypothesis we must count as many

distinct products as we can detect differentiations in spectral lines, the prospect is appalling, for this is only limited by the delicacy of our methods and the total number of lines in the spectra of all the elements.

Lockyer's explanation of the peculiarities of the calcium spectra is tenable only under the assumption that the essential differences are due solely to differences of temperature. May this assumption be granted? We think not. There is an all-important distinction between the discharge from an induction coil unmodified and when used with a condenser. To understand this distinction we must make clear to ourselves the process of discharge. The iron core of the coil is magnetized by the primary current; this current being arrested, the magnetism falls in intensity, not instantaneously, but the process occupies an appreciable time. The disappearance of the magnetism produces a difference of potential in the two termini of the coil proportional to the rapidity of the fall, which is most sudden at its beginning; if the termini are within striking distance a spark will pass, heating the insulating medium and thus lowering its resistance, so that the electro-motive force arising from the later and less rapid fall of magnetism in the core is still sufficient to overcome the lessened resistance. Thus the discharge occupies a large part of the considerable time necessary for the core to lose its magnetism. With a jar the process is quite different. Here a large amount of electricity must flow into the condenser before the potentials of the termini differ enough to disrupt the insulating medium, and when this condition is attained the core has lost the greater part of its magnetism, so the first discharge is not followed by a protracted, though decreasing current, as in the first case. Since the total amount of electricity passing in both cases is practically the same, and the heat evolved depends on the amount of electricity and the resistance, the temperature in the second case will clearly be much higher than in the first. Thus much is recognized and acted upon by spectroscopists. But suppose that besides heating intensely the medium through which the electricity passes, it be required to vaporize the material of the terminals, is there then no difference but temperature in the two cases? Most assuredly. The vaporizing of a metal is a process requiring

time as well as high temperature, and as the metal is hardly heated except at its point of contact with the heated gases of the spark, we must anticipate a much more copious evolution of vapor in the first case of slow discharge though of lower temperature. The characteristic envelope of metallic vapor about the spark of the unmodified discharge, absent or far less prominent in the condensed spark, is a familiar proof of this conclusion.

This long exposition of the nature of the electric discharge would be wholly unwarrantable did not the writer whose work we are examining, as well as other spectroscopists, seem to quite overlook its significance. Then too, we must make use of its conclusion in our reasoning.

We see then that 6, in the figure borrowed from Lockyer, represents the spectrum of calcium vapor, not only at a higher temperature than 2, but also at a less density, probably far less. It is not unlikely that the true cause of difference may be found in the latter fact.

Is it possible to explain all the phenomena cited by Lockyer, without introducing any hypothesis not rendered highly probable on other than spectroscopic grounds? Distinctly excepting the assumption that the line D_3 of the chromosphere and the line 1474 of the corona are due to hydrogen, it is.

As the foundation of this explanation we suppose granted:

1st. The essential truth of the kinetic theory of gases.

2d. That molecules are practically elastic bodies capable of vibrating in several distinct periods, and imprinting oscillations of the same period on the luminiferous ether. This necessarily implies that vibrations in the luminiferous ether of these periods may set such molecules in oscillation.

Besides this we make the sole assumption that the "damping" of these vibrations varies in the different periods, *i. e.* that the time necessary to impart all the energy of vibration to the luminiferous ether varies with the different periods. This assumption can hardly be objected to; it is quite in keeping with the conduct of other elastic bodies which are more readily studied. A tuning-fork struck by a hard body may give out a non-harmonic overtone of greater subjective intensity than the fundamental tone, but left to itself the fundamental tone survives; a cord plucked by a sharp point gives a sound, the

quality of which changes speedily by the more rapid damping of certain of its partial tones.

According to the kinetic theory, a molecule of the vapor moves onward in an essentially straight line with a velocity proportional to the square root of the absolute temperature, until it comes into collision with another, when, in general, the velocity and direction of motion are changed, and a certain portion of the energy of motion is converted into vibratory motion within the molecule. The violence of the collisions, and consequently of the intermolecular disturbance, depends upon the average velocity of the molecules, that is upon the temperature; the frequency of collision depends upon the temperature and the density of the gas.

To fix our ideas, let us suppose a simple case of a gas whose molecules are capable of vibrating in two periods α and β. Suppose again that the energy expressed in the vibrations of period α is much more quickly imparted to the ether than that embodied in the period β, *e. g.* that α would have its amplitude reduced to $\frac{1}{10}$ in a unit of time, while β would suffer a reduction to $\frac{9}{10}$ only. Now conceive this gas at such a temperature and pressure that the average interval of collision be this unit of time, the molecule would, on an average, yield 99 per cent. of its energy contained in the α period to the ether, but only 20 per cent. of that in the β period. This proportion would obtain generally, for the energy in the β period clearly could not be cumulative, a collision tending to change the sign of vibratory motion nearly as often as to simply increase the amplitude. Seen in the spectroscope the line corresponding to α would be by far the more intense; it would be the persistent line.

Imagine now, the temperature remaining the same, the density of the gas be so reduced that the average interval of collision be increased very many times. In this case the increase of energy of the α form imparted to the ether is at best but one per cent., whereas the increase in that of the β form is very great. If now the gas be spectroscopically examined (supposing the volume of gas so arranged that as many molecules send light to the collimator as before), α appears as before, but it has lost its position as the persistent line, for β is equally bright.

So much under the tacit assumption that the vibratory energy in α and β are equal. Suppose, however, which, be it noted, is not mechanically improbable, that the energy in β is the greater; then by continuing the process of rarification we have the following phenomena: first, α is the strong line, and tested as we tested hydrogen would prove the persistent line; second, α and β would be equally intense, and, tested as before, neither would be called relatively persistent; finally β would be the more intense and also the persistent line. At all times β is the *long* line. On the other hand, if α contains the greatest amount of energy it is always the most persistent as well as longest line.

Here we have derived a physical definition of a long line which may be thus stated:

The longer spectral line is that representing one of a molecule's possible vibrations which, on the average, corresponds to the greater energy.

As we have said above, Lockyer's method only determines the persistent lines under the limited range of conditions as regards temperature and pressure at his command. If to determine the long lines, the pressure be greatly reduced, the volume of the gas must be so inordinately increased, in order to secure sufficient intensity of light, that the experiment may be impossible. There is one case, however, in which we may have incandescent gases of extreme tenuity and enormous volume, namely, in the chromosphere of the sun. The relative distance, then, to which lines may be traced from the base of the chromosphere is a true expression of their relative lengths, provided that they are in the same region of the spectrum. Clearly this modification is necessary, for we may have a vibration of enormous energy to which the retina is not sensitive.

It will be seen from our point of view follows a ready explanation of the well known fact that the spectral lines increase in breadth with increased density in the gas, a phenomenon not easily explained, we think, on any other theory. Probably the period of molecular vibration, like that in other elastic bodies, is not independent of the amplitude of vibration. As the amplitude of vibration must depend on the violence of molecular collision, we should anticipate a greater proportion

of false light about a line with increased temperature. This asserts nothing about pressure. But if we recognize that the relative value of these false vibrations, since they would be rapidly damped, increases with the decrease of the mean interval of collision, the phenomenon observed follows as a necessity.

We will now as briefly as possible discuss the phenomena presented by Lockyer in the light of the preceding explanation.

The coincidences in the spectra of iron and titanium are due to impurities betrayed by long lines in the highly diluted vapors, which are not the persistent lines in the much denser vapors observed in the study of these impurities.

Calcium.

Referring to the cut, 1 and 2 are as explained; in 3 we have a large amount of vapor of considerable density, of which the centre is at a much higher temperature than the surrounding portion. At this density and temperature much of the light of the lower refrangibility is false in the sense defined above; but the colder molecules in the neighborhood readily take up the definite vibrations from the ether, and the line is reversed. The more refrangible lines are not reversed because the false light, though present, does not approach the lines in brilliancy, and thus though the lines are diminished in intensity by absorption, they are still relatively brilliant. In 4 however, by increased density of the vapor, and perhaps also by increased temperature, the lines are so widened and the colder vapor-envelope so increased in thickness that these lines are reversed in the centre. 5 requires no discussion. In 6 we have the vapor at a very high temperature, and at the same time very rare, from the nature of the discharge as explained above; the lines shown are the longest lines of the metal. Of these two the less refrangible has been proved by Young to be the longest. The observation of Huggins, which indicates that this is the only line in the spectrum of Sirius, is a proof that this vapor, copious in that star, is still extremely rare. Were these two lines due to different compounds, according to Lockyer, there is no more

reason why we should find H, the less refrangible, alone, than K, the more refrangible, but we may safely predict that the former may be found alone, or the two together, but K alone never.

Iron.

All the phenomena here discussed are explained in the simplest manner by the principles above announced. The lines observed in the chromosphere are really the long lines of the metal, at least the longest of that region of the spectrum, lines that are faint in the much denser gases studied by Lockyer because the molecule yields its energy, belonging to these periods, but slowly. If our author is driven, by the critical study of five lines, to the conclusion that iron vapor consists of no less than three elements or compounds, what may we expect when all the lines are as carefully studied?

Lithium.

As yet we have been able to find no difference between the blue and red lines of this metal, either by the discussion of the published observations, or of our own, except of luminous intensity; unless indeed one be reversed in the solar spectrum, which is more than doubtful. This difference in intensity becomes less marked at high temperatures in accordance with Fechner's law. The violet line is distinctly the longest, while the orange line is longer than the red. Yielding its vibrations more slowly to the ether, however, it becomes relatively prominent only at a very low vapor tension. The conditions required to make the latter line strong seem to have been met by the use of a coil and condenser.

In the cut illustrating the spectra of this metal there is probably a mistake in omitting the red and orange lines in the arc spectrum.

Hydrogen.

The peculiarities of the F line have already been explained. The *h* line doubtless becomes relatively prominent only with extreme tenuity and high temperature. In the alloy of indium and this element, the compound being poor in hydrogen, we

expect, from Lockyer's researches on such bodies, that the relative density of the hydrogen vapor will be very small.

On the principles here expounded we find the origin of the numberless lines in the solar spectrum, not in unknown elements which are yet to be discovered, but in the long lines of known elements which are never the persistent lines in the conditions of density and limited volume at our command.

One more point with reference to the evidence of the stars. The hotter stars are probably less advanced in evolution, hence, probably have a greater equatorial velocity than our sun. In the sun the spectrum from the approaching side is more deflected, from the receding side less deviated; if we examine the spectrum from the whole surface at once with a high dispersive power, which practically we never do, the effect would be a widening of all the lines of the spectrum with a decreasing intensity in each, in other words, quite analogous to optical confusion as produced by spherical aberration. Hence the more delicate lines would disappear. In a star we can only observe the spectrum from the whole surface. Assuming a greater equatorial velocity in Sirius, and that its axis of revolution is not directed towards us, even if its spectrum closely resembles that of the sun it would appear as it does. This assumption explains the greater width of the hydrogen lines, which must otherwise be explained on assumed greater pressure, certainly not more probable. But we will not pursue this speculation further, though we might emphasize the fact that hydrogen, that element which, according to Lockyer, even at the limited means at our disposal, is readily split up into five or six different constituents, there, even at a temperature which, according to the same authority, destroys almost all other elements as we know them, still preserves the simplest form in which we know it in our laboratory and in the chromosphere!

March 10*th*, 1879.

ON A NEW VOLUMETRIC METHOD OF DETERMINING FLUORINE.

By Samuel L. Penfield,
Assistant in the Sheffield Laboratory.

I have made the well-known reaction $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$ the basis of a volumetric determination of fluorine, estimating the quantity of hydrofluosilicic acid formed from a given weight of a fluoride by means of a standard alkali solution.

It is impossible to titrate the hydrofluosilicic acid directly, because as soon as an alkaline reaction is reached the silicofluoride is decomposed and an acid reaction is indicated, which change goes on slowly. But when barium chloride and an equal volume of alcohol are added to the solution, barium silicofluoride is precipitated from the solution, and an equivalent amount of hydrochloric acid is liberated, which can be titrated; by this means, using litmus as an indicator, I was enabled to get some very satisfactory results, but the turbidity caused by the barium silicofluoride interfered with the change of color of the litmus, and cochineal I was not able to use at all.

On further experimenting I found that potassium chloride possessed some advantages over barium chloride. On adding potassium chloride and an equal volume of alcohol, potassium silicofluoride is precipitated from the solution, and an equivalent of hydrochloric acid is liberated, but the potassium silicofluoride is a very transparent precipitate, and does not interfere with the change of color of the indicators. It is necessary that alcohol shall make up at least one-half the volume of the liquid to be titrated, so as to precipitate the potassium silicofluoride as completely as possible.

The apparatus needed is very simple, and consists of a gasometer of ten or more litres capacity, a few flasks of about 150 c. c. capacity, a few large plain U-tubes 18 centimeters long and 2½ centimeters diameter, made without any narrowing in the bend, and a heavy iron plate supported properly so that it may be heated with a lamp.

The fluoride is weighed out accurately into one of the flasks; unless it is a silicate, ten grams of powdered and ignited quartz are added, and two or three pieces of quartz about the size of kidney beans. These last facilitate mixing up the powder when the flask is shaken. The contents of the flask are then drenched with from 30 to 40 c. c. of sulphuric acid which has been previously heated and allowed to cool. The flask is tightly closed with a doubly perforated cork; from the gasometer dry air is passed into the flask by means of a glass tube which reaches nearly to the bottom. The silicon fluoride mixed with air passes from the decomposing flask first through a small U-tube, made from ordinary glass tubing, 5 millimeters in diameter, and kept cool by being placed in a beaker of cold water, then into one of the large U-tubes intended for decomposing the silicon fluoride and absorbing the hydrofluosilicic acid. The U-tube contains a solution of potassium chloride mixed with an equal volume of alcohol; the escaping gas is made to bubble through this, and to insure complete decomposition a second smaller U-tube is attached to the first: the first tube absorbs nearly all the acid, the second contains only traces. The decomposing flask is supported on the iron plate; by its side is placed a second flask containing sulphuric acid and a thermometer supported so that its bulb dips into the acid; the lamp heating the plate is placed midway between the flasks, and the heat is regulated so that the temperature of the acid remains between 150° and 160° C.

The decomposition is continued two hours in ordinary cases, and during that time a continuous current of air is forced through the apparatus, amounting to from five to six litres for the two hours, while the contents of the decomposing flask are frequently agitated by shaking.

After the decomposition and aspiration are completed the contents of the U-tubes are titrated: for this purpose they may be transferred to a beaker, the tubes being rinsed with alcohol and water, or better, the acid may be titrated directly in the U-tubes. In order that the alcohol may make up one half the volume of the liquid after the titration is completed, add a few cubic centimeters of alcohol before titrating, or where fifteen or more cubic centimeters are to be added use a standard alkali one half of whose volume is alcohol. As the

separated silicic acid sticks to the sides of the U-tube, it is necessary to have prepared a glass rod bent a little at one end to scrape off and break up this silica.

I have found by experiment that a simple dry U-tube between the decomposing flask and absorbing tube is sufficient to condense any sulphuric acid that may go over from the heated acid.

When fluorine is to be determined in a mineral containing chlorine as in the case of an apatite, substitute for the empty U-tube one filled with fragments of pumice impregnated with perfectly anhydrous sulphate of copper. This will intercept any hydrochloric acid, and will also serve to condense any sulphuric acid vapor that may go over from the heated acid. The calculation is very simple. Every one equivalent of sodium carbonate equals one equivalent of hydrofluosilic acid or six of fluorine, hence the proportion:

Mol. wt. Na_2CO_3. Mol. wt. 6 F. Amt. of Na_2CO_3. Amt. of F.

106 : 114 :: : x

Below will be found some results which I have obtained from pure fluorspar. The time of conducting the operation in every case was two hours, the amount of aspiration varied from four and one-half to six and one-half litres, and the indicator used was cochineal.

The first six were titrated with a dilute solution of ammonia, one cubic centimeter of which equalled .01242 grams of fluorine, the last four with a solution twice as strong and one-half of whose volume was alcohol.

Fluorspar.	Corresponding Weight of Fluorine.	Fluorine found.	Gain or Loss.	C. C. of Air Aspirated.
.2464	.1200	.1199	— .0001	4500
.1804	.0879	.0895	+ .0016	5000
.2039	.0993	.0989	— .0004	5500
.2384	.1161	.1169	+ .0008	5000
.2074	.1010	.1023	+ .0013	6500
.2147	.1046	.1064	+ .0018	5500
.9292	.4325	.4329	+ .0004	5500
.4673	.2277	.2283	+ .0006	6500
.9901	.4824	.4817	— .0007	6000
1.0130	.4935	.4923	— .0012	6500

March 3, 1879.

PRELIMINARY NOTICE OF AN INVESTIGATION ON "PETROCENE," A PRODUCT OF THE DESTRUCTIVE DISTILLATION OF PETROLEUM.*

By Samuel P. Sadtler and H. G. McCarter.

In the number of *Comptes Rendus* for 16th December last (tome 87, p. 991), which has just come to our notice, appears an article by MM. L. Prunier and R. David, entitled, "sur la nature de certains produits cristallisés, obtenus accessoirement dans le traitement industriel des pétroles de Pennsylvanie."

In this article the authors announce that they have begun an investigation of "Petrocene," a solid residue from petroleum, which they obtained from Dr. H. Tweddle, of Pittsburg, Pennsylvania. They give some general statements as to the several hydrocarbons, the presence of which they consider to have been indicated by the determinations they made of fusing points, boiling points, solubilities, together with crystallizations gotten with picric acid, and with binitroanthracene. Judging in this way, they state that anthracene, phenanthrene, chrysene, chrysogen and other hydrocarbons are present. They give no specific figures of analyses, but say merely that the percentage of carbon varied in their different analyses from 88 to 96 per cent. in 100. After propounding some interesting theories, based upon these indications, they close by promising to communicate the results obtained from a farther study of the subject, if, as they hoped, these should be new.

This same material has been the subject of our investigation for several months past, and we have obtained results which, while not as yet complete, are so far advanced as to be beyond the point of Messrs. Prunier and David's work, as it is stated in their article. We would therefore claim equal right to the field as scientific workers, and shall continue our studies, and hope to push them to an early completion.

* Read before the American Philosophical Society, February 7th, 1879. Communicated by authors.

The material we have operated on consists of a full set of Dr. Tweddle's preparations, as described by him in the *Franklin Institute Journal*, Vol. 72, p. 204, which was given to one of us some two years ago, by Dr. F. A. Genth, and a bottle of the crude distillate before treatment with petroleum benzine, given to us by Dr. G. F. Barker.

Some weeks of study had indeed been given to these products in the summer of 1877, by one of us in conjunction with Dr. E. F. Smith, of the University of Pennsylvania, which work was interrupted and only resumed as stated, a few months ago.

The following is a brief and general statement of the ground covered by our work. The conclusions are all subject to revision as the examination of purer products may demand.

We found that the method of breaking up the compound by treatment with solvents did not suffice to give us pure products of constant compositions. We therefore availed ourselves of the method of forming double crystallizations with picric acid from solution in alcohol and benzol. We obtained what appeared to be three distinct crystallizations here, two of deep red crystals and one of brown plates. These were picked apart as they crystallized together, using a hand lens, and exercising great care, and were then submitted to recrystallizations until quite pure and distinct. On breaking up these picric acid compounds with dilute ammonia, we obtained at least two well-marked and distinctly different hydrocarbons. With regard to the hydrocarbon from the third set of crystals we are still in doubt.

Of the two hydrocarbons, one fuses constant at 280° C., and the other at 178° C. We are not able to identify them certainly with any of the known hydrocarbons.

Of both of these hydrocarbons, quinones have been made, and of one of them the alizarine, acting upon the quinone with strong sulphuric acid with heat, and then fusing the dried residue with solid potassium hydrate. The quinone from the hydrocarbon, fusing at 280°, dissolves in sulphuric acid with a dark purple color, and when the nearly black residue of disulphoquinonic acid and potassium hydrate are fused together, a dark yellowish-brown color is obtained. From the solution of this, hydrochloric acid precipitates the alizarine as a dark brown flocculent mass.

Several analyses of this quinone and of the alizarine were made. As we hold the whole subject still open to revision, we will not quote them, but merely say that both the quinone and the alizarine derived from the hydrocarbon, fusing at 280° C., indicate a probable composition of $C_{16}H_{14}$ for the hydrocarbon. This would be a dimethyl-anthracene, yet the hydrocarbon does not agree with the dimethyl-anthracene discovered by Van Dorp, and studied by Wachendorff and Zincke.

The analysis of the other quinone gives results approximating what would be demanded by mono-methyl-anthraquinone.

Undoubtedly both hydrocarbons are slightly contaminated with chrysene or some similar hydrocarbon of higher carbon percentage, from which it is exceedingly difficult to free them.

With this brief mention of the work done, we will defer any further discussion until our results are sufficiently advanced to be presented as a whole. We are now engaged upon the work, and will push it promptly to completion.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

I.—INTRODUCTION.

By Ira Remsen.

A few years ago, in the course of an investigation on para-sulphobenzoic acid,* I made some observations on the action of potassium pyrochromate and sulphuric acid on orthotoluene-sulphonic acid and orthotoluenesulphamide, and on the corresponding compounds of the para-series, which led to the belief that the ortho-compounds are influenced by the oxidizing mixture less readily than the para-compounds. An exper-

* Amer. Jour. Sci., Vol. V., 179, 274, 354; and Annalen der Chemie, 178, 275.

iment was made with a mixture of the two isomeric sulphonic acids, and it was shown that, after treating this mixture for a long time with an excess of the oxidizing agent, a product was obtained which, on being fused with potassium hydroxide, yielded a considerable quantity of salicylic acid; and the longer the oxidation was continued the larger seemed to be the proportion of salicylic acid obtained from the product by treating it with potassium hydroxide. After proving that no ortho-sulphobenzoic acid is formed in the experiment just referred to, the statement is made: "It seems indeed from this and a subsequent experiment that the ortho-acid is acted upon with much less energy than the para-acid, if acted upon at all."

The "subsequent experiment" may be described in the words of the article in question: "That the ortho-compound in the special case under consideration is acted upon less energetically than the para-compound was also shown in a rough way by the following experiment. The potassium salts of the two sulphotoluenic acids were separated very nearly by means of crystallization. The pure para-salt was introduced into the oxidizing mixture, and the reaction that ensued carefully observed. The same quantity of ortho-salt, still containing some of the para-salt, was afterward introduced into the same quantity of the oxidizing mixture as was employed in the former case, and the reaction compared with the former one. A striking difference was observed. Whereas the reaction commenced very quickly with the para-salt, and a strong evolution of gas took place; with the ortho-salt it was necessary to apply heat for a longer time before the reaction fairly began, and then the process was markedly more sluggish, a very slow evolution of gas continuing for a long time."

Again in the study of the two toluenesulphamides a similar difference was observed. The special experiment indicating this difference was described thus: "Orthotoluenesulphamide still containing some of the paramide, was subjected to oxidation. It was immediately noticed that, as in connection with the sulpho-acids, the action in this case was not as violent as in the case of the para-compound. After heating for some time the product was examined. The parasulphaminebenzoic

acid formed was filtered off and the filtrate extracted with ether. The ethereal extract, on being distilled, left behind a residue consisting of orthotoluenesulphamide with a very little parasulphaminebenzoic acid. The latter can be readily removed by redissolving the whole in water, adding a little alkali to the solution, and then extracting with ether. In this way absolutely pure ortho-amide can be obtained. This was again subjected to oxidation, and, after treating for a length of time, no new product could be discovered in the liquid—a portion of the substance only having been destroyed. Thus we see that the conduct of the ortho-amide is exactly analogous to that of the corresponding sulpho-acid."

The results of the experiments just described led to the general inquiry whether the influence of a substituting-group, situated in the ortho-position with reference to a hydrocarbon residue, is such as always, either wholly or partially, to prevent the transformation of the residue into carboxyl by the chromic acid mixture. There are some cases on record which seem well adapted to throwing light upon this question. It has been shown, for instance, by Beilstein and Kreusler* that, when nitroxylene obtained from ordinary xylene from coal-tar is oxidized, it yields a monobasic acid, nitro-toluic acid. This acid seems to have been obtained in a pure condition. At all events the fact was established very positively that this monobasic acid is not converted into a bibasic acid by further oxidation. The authors say: "Aus obigen Versuchen ergiebt sich unzweifelhaft, dass die Einwirkung der Chromsæure auf Nitroxylol auf *eine* Methylgruppe beschrænkt bleibt. Obgleich Toluylsæure durch Chromsæure mit der grœssten Leichtigkeit kein Terephtalsæure uebergeht, widersteht die p-Nitrotoluylsæure dieser Einwirkung sehr kræftig. . . . In keinem Falle wird auch das zweite Methyl des Nitroxylols angegriffen. Die Bildung einer Sæure von der Formel der Nitro-Terephtalsæure haben wir nicht beobachtet. Offenbar bewirkt der Eintritt negativer Elemente oder Radicale in den Kohlenwasserstoff, dass derselbe widerstandsfæhiger gegen Oxydationsmittel wird. Aehnliche Erscheinungen finden sich hæufig. So wird das *Dinitrotoluol* von Chromsæure nur æusserst wenig angegriffen, wæhrend *Nitrotoluol* dadurch leicht in p-Nitroben-

* Annalen der Chemie, 144, 168.

zoesæure ueber-geht. Im *Xylol* werden beide Methylgruppen leicht oxydirt. Aber *Nitroxylol* und *Chlorxylol* liefern mit Chromsæure nur *p-Nitro-* und *p-Chlortoluylsæure*, und *Trichlorxylol* widersteht, nach den Versuchen des Herrn Vollrath der Einwirkung der Chromsæure auf das Vollstændigste."

Vollrath's experiments are described* a little later, and they show that parachlorxylene yields by oxidation parachlortoluic acid, and no bibasic acid; conducting itself just like the nitro-derivative.

Still later, Fittig, Ahrens and Mattheides in studying bromxylene showed† that it conducts itself towards chromic acid like the chlorine- and nitro-derivatives. They obtained a bromtoluic acid which, by further treatment with the oxidizing mixture, could not be converted into the corresponding bibasic acid.

It is perfectly clear from the examples referred to that the entrance of a substituting-group into xylene causes, at least sometimes, a remarkable change in the conduct of the substance towards the chromic acid mixture. One of the methyl-groups of the xylene is protected by the substituting-group against oxidation, while the other is apparently uninfluenced; and now the question would naturally arise: What position does the protecting group hold with reference to the protected methyl?

The results of my experiments on the sulpho-derivatives of toluene, as described above, would suggest that it is probably the methyl-group situated in the ortho-position which is protected in the compound, but before these experiments were performed there was nothing known that could lead to this suggestion, and no attempt indeed was made to offer any explanation of the phenomena under discussion, or to show any connection between all the cases on record in which a part of a molecule is protected from oxidation by the introduction of a negative group or groups.

After V. Meyer's‡ experiments had thrown light upon the compounds of the ortho-series, and had shown that many compounds, which had previously been considered as belonging to the meta-series, in reality belonged to the ortho-series,

*Annalen der Chemie, 144, 266. † Ibid. 147, 32. ‡ Ibid. 156, 265.

Fittig* called attention to certain peculiarities of the ortho-compounds, the most important one being the fact that "alle Ortho-verbindungen beim Behandeln mit chromsaurem Kalium und Schwefelsæure nicht die fuer die Meta- und Paraverbindungen characteristischen Oxydationsprodukte liefern, sondern ganz zerstœrt werden." He says: "Vor Allem interessant aber scheinen mir die Versuche von Beilstein zu sein, der gefunden hat, dass auch die Orthosubstitutionsproducte des Toluols, das Orthochlortoluol, das Orthojodtoluol und das Orthonitrotoluol, welche von ihm noch als Metaverbindungen aufgefasst und beschrieben sind, beim Behandeln mit chromsaurem Kalium und Schwefelsæure keine substituirte Benzoesæuren liefern, sondern verbrannt werden." Reference is also made in this article to the conduct of salicylic acid as illustrating the conduct of ortho-compounds, but I showed† subsequently that not only salicylic acid but its isomeres, oxybenzoic and paraoxybenzoic acids conduct themselves exactly like salicylic acid, and, further, that instability towards chromic acid is a characteristic of a number of aromatic oxyacids—in fact of all that were examined by me.

The impression conveyed by Fittig's article is that ortho-compounds are *less stable* than the compounds of the other series, and, hence, his interesting observation does not assist us in explaining the cases above described in which *increased stability is the result to be explained.*

It will thus be seen that the subject of the influence exerted by substituting-groups upon hydrocarbon residues contained in the same compound, as indicated by the conduct of the compounds toward oxidizing agents, was, at the time the investigations now to be described were begun, almost entirely unexamined. And it was with the distinct object of showing whether, in those cases in which a part of a molecule is protected by the presence of a negative group, a common cause could be discovered, that the investigations were undertaken. The results thus far reached all agree, and they make the conclusion extremely probable that, *in all cases now on record in which hydrocarbon residues are shown to be protected from oxidation by the presence of negative groups, the latter are in the*

*Zeitschrift für Chemie, N. F. VII, 179.

†In the article on parasulphobenzoic acid above referred to.

ortho-position with reference to the former; whereas oxidizable residues, situated either in the meta- or para-position with reference to the negative groups, are, under the same circumstances, transformed, just as if the negative groups were not present.

The oxidizing agent used, and the only one in connection with which the above conclusion holds good, is the common mixture of potassium pyrochromate, sulphuric acid and water. Other agents, such as nitric acid and potassium permanganate, act in an entirely different way, as is well known.

It is proposed then to present the results of the investigations which have led to the discovery of the principle embodied in the conclusion just stated; and, after these results have been presented, the connection between them, and their bearing upon the general subject under examination, will be discussed.

II.—ON THE OXIDATION OF XYLENESULPHAMIDES.

By Ira Remsen and M. W. Iles.

The first example selected for study was that afforded by the substitution-products of xylene. Instead of taking derivatives which had already been prepared, as the nitro-, chloro-, or bromo-derivatives, we selected, as probably better adapted to our purpose, the sulpho-compounds. As one of us had already shown that the amide of the sulphonic acid of toluene is readily oxidized, yielding a product which can be easily separated from the oxidizing mixture, and easily purified, it was thought probable that the sulphamides of xylene would be convenient substances to work with, and hence our attention was confined to these.

Preparation and Oxidation of the Amides.

The specimen of xylene from which we started was obtained by us from coal-tar oil by careful fractional distillation. It was found to consist mainly of metaxylene—the proportion of the para-compound contained in it being much smaller than is common in crude xylene. The hydrocarbon was completely converted into sulphonic acids by gently heating it on the water-bath with concentrated sulphuric acid. The solution of

the sulphonic acids in water was converted into potassium salts, by first neutralizing with finely powdered chalk, filtering from precipitated calcium sulphate, adding a solution of potassium carbonate until a precipitate was no longer formed, then filtering again, and evaporating to dryness. The perfectly dry potassium salts were then treated with an equal weight of phosphorus pentachloride, the mass being kept cool during the operation. After the action of the chloride had ceased, strong aqueous ammonia was added, and, after cooling, the precipitated amides were filtered off.

As was anticipated, it proved to be an extremely difficult and tedious operation to obtain perfectly pure substances from this mixture. Nevertheless, we finally succeeded in proving that there were three distinct amides contained in it, two of which were derived from metaxylene, and the third from paraxylene. No special description of the details of the process of separation is necessary, as it simply consisted in successive recrystallizations. On first heating the mixture with water, a portion of it was converted into an oily looking liquid, while a larger portion passed into solution. The solution was filtered off, and the solidified oil again treated with hot water. Thus more of the solid amide was extracted from the liquid; and this was again filtered off and allowed to crystallize. The crystallized portions were together treated with hot water, and a further separation of the oily liquid obtained. Thus gradually the whole mixture was divided into two portions, one of which dissolved in hot water without first fusing, while the other passed into the liquid condition before the boiling point of water was reached, and then dissolved, though with difficulty, in the boiling water. By repeated crystallizations of these two portions, two comparatively pure products were obtained. The principal portion fused in pure condition at 137° (uncorr.) and the other portion at 96-97° (uncorr.)

Both of these substances had already been obtained by Jacobsen,* and he had also shown that they are both derived from metaxylene. To show this, he heated them separately in sealed tubes with concentrated hydrochloric acid. Thus the sulphamide-group was removed and the hydrocarbon regenerated. By oxidizing this it was converted into isophthalic

*Annalen der Chemie, 184, 179; and Berichte d. deutsch. chem. Gesell. X, 1009.

acid, and its nature thus determined. We performed the same experiments with the same results. There can hence be no doubt that two sulphamides can be obtained from metaxylene, one of them fusing at 137° and the other at 96-97°, and that the one with the higher fusing point is formed in much larger quantity than the other. For convenience, we may designate the former compound as *α-xylenesulphamide*, and the latter as *β-xylenesulphamide*.

We mentioned above the presence of a third amide in the crude mixture. This substance was not formed in large quantity, and we did not succeed in preparing it in pure condition. It was found in the last mother-liquors from the crystallizations already described, and made its appearance in the form of verrucous masses without distinct crystalline structure. It fused at 143°, while according to Jacobsen* the sulphamide of paraxylene fuses at nearly 148°. Although this amide was not prepared pure by us, we succeeded in showing beyond any doubt that it is in reality derived from paraxylene. By an indirect method, which will be described later, we transformed it into paratoluic and terephthalic acids, and showed that it can be completely changed into these bodies.

The above description refers to our main series of experiments. It must be remarked, however, that we experimented upon different specimens of xylene, and, while we always found the three amides mentioned, we also obtained in more than one instance a compound which differed from these three. This we believe to have been an amide from orthoxylene, as its fusing point corresponded very nearly to that given by Jacobsen for orthoxylenesulphamide. As we only desired to study the conduct of the amides towards the oxidizing mixture, we satisfied ourselves with the preparation of the three principal ones, and then subjected them to oxidation.

Some preliminary experiments were made with the impure amides for the purpose of determining whether they yielded acids by oxidation. The mixtures at first employed consisted almost entirely of the α- and β-amides in varying proportions. Those portions which contained the largest proportions of the α-amide were oxidized much more readily than those in which the β-amide was the principal constituent, in some cases the

* Berichte d. deutsch. chem. Gesell. X, 1009.

oxidation took place with a violent evolution of gas, so that the vessel in which the operation was performed had to be cooled. In all these cases the oxidation was continued until the oil from the fused β-amide had disappeared from the surface of the oxidizing mixture. As a result of these preliminary experiments we found that a crystallized product is obtained by the oxidation of the mixtures, and that the quantity of this product varied according to the composition of the mixture. It was filtered off from the colored liquid, and washed out until the wash-water was colorless. It then appeared as a colorless, lustrous, crystallized body. It dissolved with evolution of carbon dioxide when treated with potassium carbonate, and was at least partially reprecipitated when the alkaline solution was acidified.

The formation of an acid or acids being thus established, it remained to show whether each of the amides had yielded an acid, or only one. The entire product was dissolved in dilute potassium carbonate, filtered and evaporated down to a comparatively small volume. Thus, if any of the amides should have remained unoxydized, they would crystallize out on cooling, while the sodium salt or salts, being presumably much more easily soluble than the amides, would remain in solution. In fact some amide did crystallize out. This was separated from the solution and was found to be nearly pure α-amide. The solution of the sodium salt was then acidified and the precipitated acid carefully examined. It was soon found that it consisted of but one substance which could be recrystallized from water and from alcohol. Its fusing point was found to be 247.5°-248°; and repeated crystallizations failed to change the fusing point. As will be shown below, this substance is a monobasic acid.

Some further experiments for the purpose of determining from which mixtures the largest yield of acid was produced. The yield was found to vary considerably even with the same mixture, but in general it was found that those mixtures which contained the largest proportions of β-amide yielded the largest quantity of the acid. This, taken in connection with the fact that, in a few cases in which a mixture containing a very large proportion of α-amide was oxidized, scarcely any of the acid was obtained, led to the conclusion that the acid is derived

from the β-amide. The conclusion, however, was an erroneous one, as we subsequently discovered.

On subjecting perfectly pure α-amide to the action of the oxidizing mixture, it was found to yield the monobasic acid which fuses at 247.5°–248°. The β-amide, on the other hand, is oxidized with much more difficulty, and its oxidation seems to take place in a different manner. Jacobsen mentions* an acid which he obtained in very small quantity from the β-amide. In one experiment we also succeeded in obtaining a small quantity probably of the same acid. Its quantity, however, was so small as to make a careful examination of it out of the question. From the experiments performed by us we are inclined to the opinion that if the β-amide yields a monobasic acid by oxidation with chromic acid, this acid breaks up very easily under the further influence of the oxidizing agent. Unless this is so, it is difficult to explain the facts observed by us. How shall we, for instance, explain the fact, repeatedly established by our experiments, that a mixture containing a much larger quantity of β-amide than α-amide yields by oxidation almost entirely, if not entirely, the acid of fusing point 247.5–248°? If the acid formed by oxidation of the β-amide corresponds in its properties to that formed by oxidation of the α-amide, if it is stable towards the oxidizing mixture, then we must inevitably have obtained it in considerable quantities in the course of our investigations; for, from first to last, large quantities of the amides have been oxidized by us, and in many of our first experiments we used comparatively pure β-amide. We are hence compelled to reject the conclusion of Jacobsen that the oxidation of the two amides of metaxylene takes place in essentially the same way. We believe that there are fundamental differences between the two cases; and we believe that continued and more careful investigation will hence only serve to make these differences more apparent.

Sulphaminemetatoluic Acid.

Having shown that from a mixture of the two amides one acid is produced, and that this acid can be readily obtained in

* Berichte d. deutsch. chem. Gesell., XI., 893.

pure condition, we prepared the new product in considerable quantity, and subjected it to careful study. Our method of procedure was this: The mixtures of amides were recrystallized a few times until, as already described, they were separated into a portion which fused under water, and a portion which did not liquefy on being heated under water. The portions of lower fusing point were first oxidized. The proportions used were: 22 grams amide, 106 grams potassium pyrochromate, and 160 grams concentrated sulphuric acid, diluted with three times its volume of water. This mixture is introduced into a flask connected with an inverted condenser, and then gently heated upon a sand-bath. In a short time an agitation is noticed on the surface of the liquid; now the flame is removed. The activity of the reaction increases, and proceeds for some time without the application of heat. When the liquid becomes quiet, heat is again applied, and the whole kept in gentle boiling for about twelve hours. The amount of time necessary to complete the oxidation varies with the composition of the mixture, so that no general directions can be given in regard to the time. In each case, it is safe to continue to apply heat until all the oil resulting from the fusion of the β-amide has disappeared from the surface of the oxidizing mixture.

After the process is completed, and the mixtures have cooled down, the product will be found in crystallized form. It is now filtered off and separated from unoxidized amides, by the method above described. It is dissolved in dilute sodium carbonate, filtered and evaporated down to a comparatively small volume. On cooling, the unchanged amide crystallizes out. Usually very little is obtained. The solution of the sodium salt of the acid is acidified with hydrochloric acid. The precipitated acid filtered and carefully washed with cold water, and then recrystallized from water.

After the oxidizing mixtures are filtered off, they still contain some of the new acid. A considerable quantity of this can be obtained by allowing the solutions to evaporate somewhat on the water-bath, when, on cooling, the acid will be deposited. There is still contained a small quantity of another acid in the concentrated oxidizing mixtures. This is not, however, as has been indicated, isomeric with the acid now specially

under consideration. As will be shown further on, it is a result of further oxidation of the first product.

After one or two crystallizations from water the new acid is perfectly pure. Its analysis showed it to have the composition, $C_8H_9SNO_4$.

I.—0.231 grams of the acid fused with potassium hydroxide and then treated with bromine water according to the method recently described by Fahlberg and Iles* gave 0.252 grams $BaSO_4 = 0.0345996$ grams S.

II.—0.28475 grams of the acid treated in the same way gave 0.30822 grams $BaSO_4 = 0.042318$ grams S.

III.—0.2865 grams of the acid treated, according to Liebig's directions, with potassium hydroxide and saltpeter, gave 0.31497 grams $BaSO_4 = 0.043245$ grams S.

IV.—0.44905 grams substance gave 27.2 cc. N at 759.5 mm. pressure, and 24° C.

V.—0.59615 grams substance gave 35 cc. N at 761.5 mm. pressure, and 19° C.

	Calculated.		Found.				
			I.	II.	III.	IV.	V.
C_8	96	44.65	...	...	...	...	...
H_9	9	4.19	...	...	...	...	...
O_4	64	29.77	...	...	...	...	...
N	14	6.51	...	...	...	6.78	6.75
S	32	14.88	14.98	14.86	15.09	...	...
	215	100.00					

The results of these analyses, taken together with those to be given of the salts of the acid, prove conclusively the correctness of the formula accepted.

The acid is hence seen to be derived from the amide by the oxidation of one of the methyl groups.

The amide being $C_6H_3\begin{cases}CH_3\\CH_3\\SO_2NH_2\end{cases}$, the acid is $C_6H_3\begin{cases}CH_3\\COOH\\SO_2NH_2\end{cases}$.

As the xylene from which the amide is derived is meta-xylene, the acid which would be formed from it by the oxidation of one methyl-group would be metatoluic acid. Hence the name of the new acid is *sulphaminemetatoluic acid.*

* Berichte d. deutsch. chem. Gesell. XI, 1187.

Sulphaminemetatoluic acid is comparatively easily soluble in hot water, but difficultly soluble in cold water. In hot alcohol it is easily soluble, in cold less readily, but still not difficultly. It is nearly insoluble in ether, both warm and cold. In cold chloroform it is insoluble, in warm but slightly. Finally in both warm and cold carbon bisulphide it is insoluble. From the solution in hot water it crystallizes on cooling in peculiar, thick, pointed, prismatic crystals which occasionally attain a considerable size. Sometimes it crystallizes in very long, lustrous, thick needles, but the two forms have exactly the same fusing point. The fusing point is 247.5-248° uncorrected, and 254.5-255° *corrected*.

A large quantity of the acid was prepared by us in perfectly pure condition. We took every precaution to insure its purity, and always carefully tested every portion used for different experiments. In order to characterize the acid a number of its salts were prepared and analyzed.

Barium sulphaminemetatoluate, $(C_6H_3.SO_2NH_2.CH_3.COO)_2Ba + 5H_2O$, was prepared by boiling the free acid with pure barium carbonate. It is very easily soluble, but from the concentrated solutions it separates in a compact mass which consists of very fine silken needles. The crystals dried in the air were analyzed.

I.—0.3865 grams dried salt gave 0.158 grams $BaSO_4$ = 0.092904 grams Ba.

II.—0.157 grams dried salt gave 0.06475 grams $BaSO_4$ = 0.03807 grams Ba.

III.—0.1815 grams salt lost 0.025 grams H_2O at 200°.

IV.—0.1360 grams salt lost 0.01888 grams H_2O at 180°.

	Calculated.		Found.			
			I.	II.	III.	IV.
$(C_8H_8SNO_4)_2$	428		...	...	...	...
Ba	137	24.25*	24.04*	24.25*	...	...
5 H_2O	90	13.74	...	...	13.77	13.88
	655					

Calcium sulphaminemetatoluate, $(C_6H_3.SO_2NH_2.CH_3.COO)_2Ca + 1\frac{1}{2}H_2O$, was prepared by boiling a solution of the acid with finely powdered Iceland spar. It is easily soluble in water,

*Calculated for dried salt.

and crystallizes in small concentrically arranged needles. After drying in the air, it was analyzed.

I.—0.3620 grams salt lost 0.0195 grams H_2O at 200°, and gave 0.101 grams $CaSO_4$.

II.—0.3145 grams salt lost 0.0170 grams H_2O at 195°, and gave 0.0875 grams $CaSO_4$.

	Calculated.		Found. I.	Found. II.
$(C_6H_5SNO_4)_2$	428	86.47	...	...
Ca	40	8.08	8.21	8.18
$1\frac{1}{2}H_2O$	27	5.45	5.39	5.40
	495	100.00		

Silver sulphaminemetatoluate, $C_6H_3.SO_2NH_2.CH_3COO\,Ag$, was prepared by adding silver nitrate to a solution of the ammonium salt. It is precipitated in flocculent masses, which may, however, be obtained in the form of needles by recrystallization from water. The air-dried salt was analyzed.

I.—0.083 grams salt gave 0.02775 grams Ag.

II.—0.10125 grams salt gave 0.03375 grams Ag.

	Calculated.		Found. I.	Found. II.
$C_6H_5SNO_4$	214	66.46	...	...
Ag	108	33.54	33.43	33.33
	322	100.00		

Sodium sulphaminemetatoluate is very easily soluble in water and crystallizes in delicate needles.

Copper sulphaminemetatoluate, prepared by precipitating the barium from a solution of the barium salt by means of copper sulphate, can be obtained, by careful evaporation, in delicate radiating needles of a blue color. If evaporated by boiling, the salt is partly decomposed, and a light blue, difficultly soluble powder is thrown down.

Cobalt sulphaminemetatoluate crystallizes in small round, very compact, radiating needles. It is easily soluble in water.

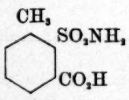
When heated with concentrated hydrochloric acid in a sealed tube up to 220° sulphaminemetatoluic acid is decomposed entirely with a separation of free carbon. At 150° it is also completely decomposed. Special experiments were under-

taken to determine the temperature at which the decomposition takes place. If the substance is not heated above 130°, the acid separates unchanged on cooling. If heated up to 140° decomposition takes place. It was not possible to obtain metatoluic acid from it by this means. Experiments with dilute hydrochloric acid gave similar results; no metatoluic acid could be obtained. It will be seen later that this conduct is entirely different from that shown by an isomeric acid, sulphamineparatoluic acid.

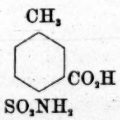
Structure of Sulphaminemetatoluic Acid.

For the purpose of this investigation it was of the first importance for us to determine, by the application of all of the methods at our command, the structure of the new acid. The method of formation leaves no doubt in regard to the relative positions of the methyl and carboxyl groups with reference to each other. They are in the position designated as meta. It remains, however, to decide in what relation the sulphamine-group stands to the two other groups in the benzene-nucleus. According to the commonly accepted hypothesis in regard to the nature of benzene-derivatives, four isomeric sulphamine-metatoluic acids are possible. These may be conveniently represented by the following schemes:

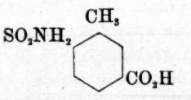
I.



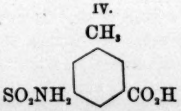
II.



III.



IV.



It must be borne in mind that the facts expressed by these formulas might be expressed equally well in ordinary language, and that the only object in using them here is for the sake of brevity. The proofs which will be offered for the structure of the acid under discussion are not dependent for

their validity upon the acceptance of any hypothesis. They would be equally valid no matter what hypothesis we might hold in regard to the nature of benzene and its derivatives.

On examining the formulas given, it will be seen that, in the first, the sulphamine-group is represented as occupying the same position with reference to both the other groups, and, as the carboxyl-group has undoubtedly been formed by direct oxidation of the original second methyl-group of the amide, in the latter compound the sulphamine-group must have occupied the same position with reference to both methyl-groups. The same statement holds true in regard to formula IV., and the original amide of the acid represented by it. It would seem probable that, if oxidation of either methyl should take place readily in these two amides, the second methyl would also be oxidized, and that in both cases the chief product of the oxidation would be a bibasic acid, while, of course, as an intermediate product, some of the monobasic acid resulting from oxidation of only one of the methyl-groups would probably be obtained. It is difficult, however, to speculate upon this subject. It is possible that the process would take place in an entirely different way. Possibly one of the methyl-groups might be oxidized completely at first, and then by its presence in the molecule prevent the further oxidation. There are some facts known which seem to point to this latter as the true view of the matter; but there are not enough facts known to warrant us in expressing anything like a decided opinion at present.

As regards formulas II. and III., the acids represented by them are derived from the same amide. If II. represents our acid, then the ortho-methyl group must have been oxidized and the para-methyl protected. But this would not be at all in harmony with the facts discussed in the introduction to this memoir. There is no case known in which a para-methyl group is protected from oxidation; and, further, when these investigations were begun there was no case known in which an ortho-methyl-group was oxidized by the chromic acid mixture. If, on the other hand, our acid has the structure represented by formula III., then the ortho-methyl has been protected and the para-methyl oxidized; and this would be in accordance with known facts. It will be shown that this formula actually represents the structure of our acid.

Transformation of Sulphaminemetatoluic Acid into Oxytoluic Acid (Orthohomoparaoxybenzoic Acid).

The conversion of the sulphamine-group, SO_2NH_2, into hydroxyl can be effected very readily. Indeed it seems to take place better than the same conversion of the sulpho-group. The potassium salt of sulphaminemetatoluic acid was made, and its solution evaporated nearly to dryness, so that, on cooling, it formed a pasty mass. This was then gradually added to about twenty parts fused potassium hydroxide, contained in a large silver crucible. The mass was kept in fusion by the aid of a small flame until ammonia ceased to be evolved, and during this time it was continually stirred with a silver spatula. After cooling, the contents of the crucible were dissolved in a relatively small amount of water, and the solution, which was almost colorless, acidified with dilute hydrochloric acid. A voluminous white precipitate was immediately formed, and sulphur-dioxide escaped. The precipitate, after being filtered off and carefully washed out with cold water, was dissolved in hot water in which it is quite easily soluble. On cooling, this solution deposited the new acid in beautiful, long, lustrous needles, which, in their general appearance, suggest salicylic acid. The acid exhibited the properties of a pure substance, such as crystalline form, constant fusing point, &c., and, hence, it was at once analyzed. On drying at 100° it was found to become opaque, and this change was shown to be due to the escape of water of crystallization.

0.2925 grams substance lost 0.0172 grams H_2O at 130°.

	Calculated.		Found.
$C_8H_8O_3$	152	94.41	...
$\frac{1}{2}H_2O$	9	5.59	5.88
	161	100.00	

0.1605 grams substance, dried at 100°, gave 0.07925 grams H_2O; and 0.3700 grams CO_2.

	Calculated.		Found.
C_8 ...	96	63.16	62.87
H_8 ...	8	5.26	5.49
O_3 ...	48	31.58	31.64
	152	100.00	100.00

The analyses thus show that the substance has the composition of an oxytoluic acid containing half a molecule of water of crystallization in its molecule. It is $C_8H_8O_3 + \frac{1}{2}H_2O$.

The acid is difficultly soluble in cold water, but easily in hot water. The solution is not colored by ferric chloride. It is easily soluble in alcohol and ether; insoluble in carbon bisulphide, cold as well as hot; insoluble in cold chloroform, difficultly in boiling chloroform. It crystallizes from water in long, beautiful, very fine needles with a silken luster. With its water of crystallization it melts at 146.5°-147° (uncorr.) After the loss of its water, its fusing point is 170.5°-171° (uncorr.), or 174°-175° corrected. The acid, after the water of crystallization is driven off, is brittle and without luster. It is not volatile with water vapor. It sublimes easily, and is deposited in the form of interlaced needles: These fuse at 165°-166°. The low fusing point indicates a slight decomposition under the influence of the heat.

Calcium oxytoluate, $(C_6H_3.OH.CH_3.COO)_2Ca + 3H_2O$, was prepared by boiling the acid with finely powdered Iceland spar. It is easily soluble in water, and crystallizes from a concentrated solution in small, spherical masses which are composed of microscopic needles.

I.—0.16825 grams salt lost 0.02307 grams H_2O at 130°; and gave 0.581 grams $CaSO_4$.

II.—01177 grams salt lost 0.01605 grams H_2O at 130°; and gave 0.0404 grams $CaSO_4$.

	Calculated.		Found.	
			I.	II.
$(C_8H_7O_3)_2$	302	76.26	..	...
Ca	40	10.10	10.16	10.09
$3H_2O$	54	13.64	13.71	13.64
	396	100.00		

Barium oxytoluate, $(C_6H_3.OH.CH_3.COO)_2Ba + 3H_2O$, was prepared by boiling the free acid with pure barium carbonate. It is not as easily soluble as the calcium salt. It crystallizes in spherical masses which have a mother-of-pearl luster.

I.—0.19675 grams salt lost 0.021 grams H_2O at 120°; and gave 0.09325 grams $BaSO_4$.

II.—0.1604 grams salt gave 0.07585 grams $BaSO_4$.

III.—0.14275 grams salt lost 0.1525 grams H_2O at 120°.

IV.—0.235 grams salt lost 0.026 grams H_2O at 155°.

	Calculated.		Found.			
			I.	II.	III.	IV.
$(C_8H_7O_3)_2$	302	61.26	...	...	...	...
Ba	137	27.79	27.87	27.81	...	...
$3H_2O$	54	10.95	10.67	...	10.68	11.06
	493	100.00				

The barium salt is decomposed at 160°.

Manganese oxytoluate, $(C_6H_3.OH.CH_3.COO)Mn + 2H_2O$, was prepared by boiling the free acid in water with manganese carbonate. It is very easily soluble in water, and crystallizes in small, compact prisms of a light brown color.

I.—0.19765 grams salt lost 0.01825 grams H_2O at 160°; and gave 0.0391 grams Mn_3O_4.

II.—0.220 grams salt lost 0.02085 grams H_2O at 160°; and gave 0.04325 grams Mn_3O_4.

	Calculated.		Found.	
$(C_8H_7O_3)_2$	302	76.85	...	...
Mn	55	13.99	14.25	14.16
$2H_2O$	36	9.16	9.23	9.48
	393	100.00		

Copper oxytoluate, $(C_6H_3.OH.CH_3.COO)Cu + 1\frac{1}{2}H_2O$, was prepared by adding a solution of copper nitrate to a solution of barium oxytoluate. A flocculent, blue precipitate separates immediately. This precipitate dissolves in hot water, and, on cooling, the solution deposits beautiful, dark green, compact prisms. Sometimes by slow crystallization from a dilute solution, large groups of compact prisms are formed. The salt is difficultly soluble in water. It is the most characteristic of the salts of oxytoluic acid examined by us.

I.—0.143 grams salt lost 0.0102 grams H_2O on being heated up to nearly 200°.

II.—0.1113 grams dried salt gave 0.02265 grams CuO.

III.—0.1113 grams dried salt deposited 0.0184 grams metallic copper by the electrolytic method.

	Calculated.		Found.		
			I.	II.	III.
$(C_8H_7O_3)_2$	302	76.96	...	...	...
Cu	63.4	16.16	...	16.24	16.53
$1\frac{1}{2}H_2O$	27	6.88	7.13	...	...
	392.4	100.00			

Silver oxytoluate is precipitated as a flocculent mass on adding silver nitrate to a solution of the ammonium salt. If this precipitate be dissolved in water it is deposited, on cooling, in the form of beautiful compact crystals. This salt was not analyzed.

When treated with nitric acid the oxytoluic acid under consideration is converted into a yellow compound which can be obtained in crystallized form from a solution in water. This is probably a nitro-compound. As yet we have not studied any more derivatives of the acid.

[*To be continued.*]

REVIEWS AND REPORTS.

ON AN APPLICATION OF THE NEW ATOMIC THEORY TO THE GRAPHICAL REPRESENTATION OF THE INVARIANTS AND COVARIANTS OF BINARY QUANTICS. By J. J. Sylvester. American Journal of Mathematics, Vol. I. p. 64.

There is a conviction in the minds of chemists, that at some future time, when the theory of chemistry shall have been developed, the intricate phenomena of the science will become expressible in the perfect language of mathematics, just as at present it is possible thus to express the phenomena of electricity, of light, of heat.

Hence any indication of the possibility of applying mathematics to the discussion of the problems of chemistry must be hailed with delight by those who are accustomed to think upon these problems.

As an indication of this kind we call attention to the extremely interesting article the title of which is given above. It is true the author does not himself propose to apply mathematics to chemistry, but, strange as it may sound, he proposes to make use of the common chemical formulas to express mathematical truths. The fact that this latter application is possible indicates, however, that there exists an analogy between certain facts which the mathematician desires to express and those which the chemist has to deal with.

The author's own language will more forcibly convey the idea which he has in mind than anything we can say:—"Impressed as I had long been with a feeling of affinity, if not of identity, of object between the inquiry into compound radicals and the search for 'Grundformen' or irreducible invariants, I was agreeably surprised to find, of a sudden, distinctly pictured on my mental retina a chemico-graphical image serving to embody and illustrate the relations of these derived algebraical forms to their primitives and to each other."

While we cannot pretend to a knowledge of the branch of mathematics to which reference is here made, we may by means of a few quotations make clear the character of the analogy thus discovered.

"Any binary quantic," says Professor Sylvester, "may be denoted by a single letter with a number attached corresponding to its degree, and may therefore be adumbrated by a chemical symbol, with corresponding *valence*. Thus hydrogen, chlorine, bromine, or potassium, will serve to denote so

many distinct binary linear forms; oxygen, zinc, magnesium, etc., binary quadrics; boron, gold, thallium, cubics; carbon, lead, silicon, tin, quantics; nitrogen, phosphorus, arsenic, antimony, etc., quintics; sulphur, iron, cobalt, nickel, etc., sextics.

"The factors of any algebraical form may be regarded as in some sense the analogues of the rays of atomicity in the equivalent chemical atom—these rays being what Dr. Frankland, according to his nomenclature, would have to designate as free bonds; such rays between two consecutive atoms in a molecule are conceived as blending in some manner so as to represent some unknown kind of special relation existing between them; they may then with propriety be called bonds or lines of connexion.

"An invariant of a form or system of algebraical forms must thus represent a saturated system of atoms in which the rays of all the atoms are connected into bonds. Thus *e. g.* O_2 . . . will represent a quadratic invariant of a quadric. . . . Potash, . . . having for its graph K—O—H, will represent the invariant to a system of one quadratic and two linear forms which is linear in each set of coefficients."

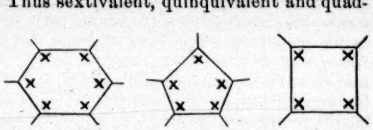
The author illustrates the analogy by a number of examples. In speaking of the formula benzol, he says:—"As, however, the question is one purely of colligation or linkage in the abstract, it is sufficiently described as a hexagon in which the three pairs of opposite angles are joined; or, if we please, as two triangles, in which each angle of one is connected with a corresponding angle of the other. In regard of the atomicity theory, all these modes of colligation are identical, and the supposition that there is any real difference between them, or that figures in space are distinguishable from figures in a plane (as I heard suggested might be the case by a high authority, at a meeting of the British Association for the Advancement of Science, where I happened to be present) is a departure from the cautious philosophical views embodied in the theory as it came from the hands of its illustrious authors, and continued to be maintained by their sober-minded successors and coadjutors, and affords an instructive instance of the tendency of the human mind to the worship, as if of self-subsistent realities, of the symbols of its own creation."

This passage serves to show that Professor Sylvester has a much clearer idea of the scope and real meaning of the so-called structural formulas, or, as he well calls them, "chemicographs," than many chemists have. The words: "The question is one purely of colligation or linkage in the abstract," should be used with emphasis whenever the dangerous task is undertaken of explaining to beginners the meaning and use of the formulas. Misapprehension in regard

to this point is really the cause of most of the objection that is raised to structural formulas by persons who have not very thoroughly familiarized themselves with the process of evolution which has led very naturally to the conceptions at present held by the leading chemists of the world. Indeed some of the most telling objections raised have been based in a vague sort of way upon the idea that the formulas did violence to certain (undefined) mathematical truths. It is, hence, doubly interesting to find a mathematician using the language which we have above quoted.

In another passage the same idea is expressed in a different way: "Chemical graphs, at all events for the present, are to be regarded as mere translations into geometrical forms of trains of priorities and sequences having their proper *habitat* in the sphere of order and existing quite outside the world of space."

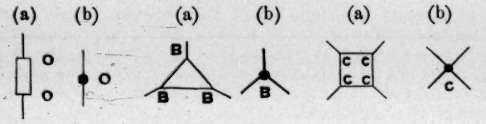
The conception of variable valence which causes so much difficulty for chemists finds no analogy in algebra, but Prof. Sylvester recognizes this difficulty, and proposes an hypothesis for the purpose of explaining the variability. This hypothesis is certainly much more satisfactory than any that has thus far been proposed; though it is well to bear in mind that those hitherto proposed scarcely deserve the name of hypothesis. "It is this: leaving undisturbed the univalent atoms, let every other n-valent atom be regarded as constituted of an n-ad of *trivalent* atomicules arranged along the apices of a polygon of n sides. Thus sextivalent, quinquivalent and quadrivalent atoms in their maximum valence will be represented by the adjoining figures where the letters denote *trivalent atomicules.*



When the valence is reduced by two we need only conceive any one of the side loops doubled or a new loop as formed by the coalescence of a pair of free bonds or tails. . . . We have thus a conceivable and conformable-to-analogy method of accounting for the variability in question. So likewise, a trivalent atom with maximum state of valence will be represented by figure 1 and when univalent by figure 2 This hypothesis of atomicules, if unobjectionable on other grounds, would not be open to the charge of having any tendency to disturb or complicate the existing graphology; for we should still be at perfect liberty to substitute for the graphs (a) of the subjoined figures the abridged notation (b), and should naturally

1

2



do so when considering the relations of atoms to each other. The beautiful theory of atomicity has its home in the attractive, but somewhat misty, borderland lying between fancy and reality, and cannot, I think, suffer from any not absolutely irrational guess which may assist the chemical enquirer to rise to a higher level of contemplation of the possibilities of his subject."

In a letter to Prof. Sylvester, by Dr. Frankland, published in the *Amer. Journ. Mathematics*, Vol. I. p. 345, reference is made to the hypothesis just described in the following words: "It seems to me that your conception of the constitution of atoms may prove of great value, not in its application to variation of atomicity, but in furnishing an explanation of the behavior of certain atoms which has long puzzled me and doubtless also other chemists. Carbon affords the best example of what I mean. The strong affinity of carbon for carbon is a quality upon which depends the very existence of nearly every organic compound, and sharply distinguishes these compounds from the almost equally complex siliceous minerals, in which the atoms of silicon are, in no single instance, combined with each other. The most obvious explanation would be that the bonds of carbon are + and — to each other, whilst those of silicon are identical or endowed with energy of the same kind and intensity. But it is a remarkable fact that hitherto, with very few and dubious exceptions, all attempts to establish a difference between the four bonds of the carbon atom have failed. Thus, if an atom of carbon be combined with four atoms or monad groups, a, b, c, d,

$$\begin{matrix} & +b & \\ & | & \\ -c- & C & -a+ \\ & | & \\ & -d & \end{matrix}$$

and c and d —, it does not matter apparently in what order these bodies are introduced to the carbon atom; for instance, if the body +a be replaced by a negative body —c, and —c by a + body +f; and if then in another molecule of

$$\begin{matrix} & +b & \\ & | & \\ -c- & C & -a+, \\ & | & \\ & -d & \end{matrix}$$

—c be replaced by —e and +a by +f, the two new molecules are identical and not isomeric as might be expected. But if, according to your conception, each bond is tripartite, it could, of course, exert either + or — energy according to the quality of the atom or group presented to it."

We must confess that to us there is something very attractive in this hypothesis of "atomicules." Not that it gives a full and satisfactory explanation of the numerous puzzling

facts known to chemists, which have always interfered with the acceptance of the idea of valence; but it approaches more nearly to a working hypothesis than any idea that has as yet been proposed. It seems possible that experimental methods now in use may, if properly applied, enable us to test the accuracy of the hypothesis.

Some such possibility is suggested by the remarks* of Prof. Mallet on the paper under consideration. In these remarks, attention is called to the fact that the conversion of ozone into ordinary oxygen is accompanied by an evolution of heat. The ordinary graphs for oxygen and ozone do not offer any explanation of this fact, for the number of bonds for each atom and the average distance between it and the other atoms with which it is connected is just the same in O=O and in

(Ordinary Oxygen) (Ozone.)

On the other hand, by means of the graphs of Professor Sylvester, a possible reason for the observed thermal relations can be discovered. For "the average distance between the atoms, as also between the atomicules, is increased in passing from the ordinary form of oxygen to ozone; or, in other words, the production of ozone from oxygen gas is an act of *partial* chemical decomposition,† not resulting in the detachment of the constituent atoms from each other; on the contrary, leaving them in a state of definite chemical combination, but removed further apart than they were in the more stable form of the element; hence, as in complete, so in this which I have called partial decomposition, extraneous energy is necessary; while the reverse change, from ozone back to ordinary oxygen, is an act of more intimate chemical union, resulting in closer approximation of the constituent parts of the molecule, and hence attended with evolution of energy, as in the form of heat."

Similar observations in connection with the allotropic forms of phosphorus, and possibly also with the different varieties of sulphur, might throw some light, though it would be but faint, upon the hypothesis of "atomicules." It is not probable, however, that any very satisfactory experimental evidence, either for or against the existence of atomicules, can be given. Whether, after almost infinitely more is known than is at present known, in regard to the conduct of substances towards one another under the most varied circumstances, it will be possible by mathematical reasoning to pierce the veil which now hides from us the structure of matter, is a question which cannot be positively answered. But the attempt to answer it will necessarily reveal to us very clearly our present position.

EDITOR.

*Amer. Journal Mathematics, Vol. I. p. 277.

† The word *deformation* has been suggested to us to express this idea.—ED.

Lecture Notes on Chemical Physiology and Pathology. By Victor C. Vaughan, M. D., Ph. D. Pp. 315. Ann Arbor Printing and Publishing Company.

This book is an unusually good one of its kind. Of course a treatise on physiological chemistry which almost entirely avoids the consideration of the chemical processes going on in the living body (containing, for instance, hardly any reference to such important questions as the sources of animal fats and of glycogen), is very incomplete. But we imagine that practically no one will be deceived by the title. It has somehow come to pass that the study of the proximate and ultimate constituents of the dead body, the composition of the secretions of the living body, and some account of the chemistry of digestion, are considered the end and aim of physiological chemistry, and on such points the information given by the author is tolerably full and more accurate than common. The selection of topics has no doubt been largely influenced by their fitness for practical study in the laboratory and to a certain extent by their importance to the medical practitioner: thus more than half the book is devoted to the consideration of the urine. But on any principle of selection we find it hard to account for the absence of even a brief account of the gaseous interchanges occurring in respiration; since in the hands of Pettenkofer and Voit and others they have thrown more light than any other material exchanges between the living animal and its environment upon the chemical processes in the body in rest or work and on different diets. At least rough quantitative examination of the inspired and expired air could be carried on by most students; and we think the more advanced might well be taught something of the mode of examining the blood gases.

The great bulk of the work is of course a compilation, but in several subjects the author records experiments made on himself or on his students with their co-operation. Those on the relationship of the daily urea excretion to the kind of food eaten and to muscular work, although they give no new results, are especially welcome now, when under the powerful influence of Flint there seems some danger in this country of a revival of Liebig's erroneous views. The concise critical statement of the question given by the author will also be useful, and under present circumstances we would have been glad to see it expanded.

Of errors we have detected but few. One is the statement that Kühne has proposed the terms antipeptone and hemipeptone as equivalent to the parapeptone and peptone of Meissner. In fact Kühne strives to show that parapeptone is not a product of normal digestion at all, but that under the influence of the gastric secretion two groups, which he calls the *anti* and *hemi* groups, are produced by the splitting up,

with hydration probably, of albuminous bodies, which latter he considers to contain anti- and *hemi-* residues. If this view be correct, it is of such importance as giving the first clue to the constitution of this class of bodies, that we think some space might well have been devoted to an account of it.

It will, however, be so much of a novelty to have a physiological chemistry of manageable size and general accuracy, to place in the hands of students as a guide in their laboratory work, that we have no doubt Dr. Vaughan's book, in spite of its faults, (which are nearly all of the easily condonable type of sins of omission) will be welcome wherever there is a physiological laboratory.

H. Newell Martin.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years. By J. W. Mallet.

A thoughtful survey of the varying uses made by man of the forms of matter which surround him, and of the different methods by which he works these materials and fits them to his service, is always interesting. The ample and valuable reports upon the progress of industrial chemistry which appear nowadays at frequent intervals are not simply useful to the manufacturer engaged in each special branch of industry, but may be read with pleasure and profit by the student of scientific chemistry, who can look beyond the mere results of experience and trace the history of principles side by side with that of their application; and by the well educated general reader, who may see spread before him one field, and that not a small one, of our expanding domain over external nature, the domain which constitutes our material civilization.

The very thoroughness, however, with which the best reports of this kind are prepared makes it somewhat difficult to obtain from them a broad, general picture of the condition of chemical industry from time to time. One's attention is taken up and one's memory wearied by the multitude of details, a large proportion of which are of subordinate or temporary importance, while the transition from one great phase of a manufacture to another is thus rendered less noticeable; just as, when one becomes entangled in the movement of a great army, the impression of endlessly succeeding men and horses and individual commands makes it far from easy to obtain any general idea of the main direction taken or the changes in the positions taken up. It may, therefore, be worth while to attempt a short, condensed sketch of the principal changes which the last few years have brought about in the condition of the manufactures most

dependent upon chemistry, overlooking the slow and often uncertain steps by which results have been reached, and the smaller details of improvement in the results themselves. Such a sketch must of necessity include matters for the most part familiar to all those whose attention has been given to this class of subjects, but need not on that account be without interest even for such.

It is not easy, nor is it necessary, to define with exactness what is meant by thus speaking of the "last few years." Different industries do not advance *pari passu*, and the position in which one is found at present may be essentially that which it assumed twenty or twenty-five years ago, while another may have undergone an important change within two or three or ten years, and a third may be now in the very act of transformation. It best answers the purpose aimed at to note for each the chief features of its present condition and most recent changes of importance. In some directions little or nothing is to be observed of really noteworthy progress, the history of a manufacture for a long time past involving either merely improvements in small though perhaps useful details, or attempts at new processes tried for a while and then allowed to pass out of use as unfit to replace older methods.

In such a general survey as is proposed, the salient points most attracting attention may be classified somewhat as follows:

I.—Improvements in the attainment of old results; depending on:

1. New sources of supply of long known materials.
2. Introduction of new materials.
3. New processes involving either new principles or modifications in the application of old ones.
4. New mechanical appliances.

II.—Attainment of new results arising from:

1. New means of production.
2. New demands from consumers.

III.—Disposition made of:

1. Old and
2. New secondary products or waste materials.

IV.—New and special conditions of work, as:

1. Changes in labor market.
2. Changes in legislation, taxation, tariffs, &c.
3. Exceptional demands for particular products, as under stress of war, blockade, &c.

V.—Problems:

1. Long outstanding.
2. Recently suggesting themselves, which still await solution.

As regards the several departments of industry which may

be claimed as chemical, or closely related to chemistry, they will be run over pretty nearly in the order in which the writer has been in the habit of discussing them in annual lectures to one of his classes of students.

Fuel, and Arrangements for the artificial Production of Heat.

Under this head we may fairly place foremost in importance among still recent improvements the admirable gas furnace of Siemens. The invention, in its practical shape, involves two distinct ideas. First, the production by simple, readily controlled means, and from cheap, even refuse forms of combustible matter of a purely gaseous fuel, the supply of which to the furnace can be regulated as easily as by turning a stop-cock, while all injury to the material heated arising from soot, ashes and unburnt particles of solid fuel is completely obviated; secondly, the arrangement of a hearth in which this gas may be burned in admixture with air after both have been separately raised to a high temperature by passage through heated chambers filled with loosely piled fire-brick, while the heating of a second pair of such chambers, through which the gas and air may be turned after the others have cooled down, is accomplished by leading through them on the way to the chimney the products of combustion from the other end of the hearth. By shifting the dampers or valves at intervals the air and gas supply is transferred from one end of the hearth to the other, one pair of fire-brick chambers being always engaged in storing up heat which otherwise would go to waste with the draft up the chimney, while from the other pair such accumulated heat is taken up by the gaseous fuel and air on their way to the hearth. In fact we have here essentially the principles of the "oxyhydrogen blow-pipe" and the "hot blast" combined and applied in simple form and upon a grand scale. As to the temperature so producible, it may be said that its practical limit is found in the difficulty of getting material infusible enough for the hearth lining, while the actual temperature at which the furnace is worked may be regulated by simply turning on or off the valves which control the admission of gas and air, and with a precision far beyond that which depends upon any mechanical stoking of solid fuel. And, most difficult object of all to attain with any of the older forms of furnace, and of great importance often from the chemical point of view—the *relative* supplies of combustible gas and air may be easily so adjusted by using the respective valves independently as to yield in the hearth an oxidizing, a reducing, or a perfectly neutral atmosphere.

Whether in connection with the "regenerator" gas furnace or the old-fashioned reverberatory, a most useful labor-saving

appliance of comparatively recent years is the rotating hearth, a cylindrical or barrel-shaped vessel of iron lined with infusible material which is slowly revolved about its axis of figure by gearing on the outside, while through it from end to end passes the flame on its way to the chimney; the material to be heated being turned over and over, its different parts mixed, and fresh surfaces exposed to the flame, without the necessity for severe manual labor on the part of workmen with iron bars, and without the exposure to air which the introduction of these bars entails.

The simplicity and economy with which combustible material, otherwise of small value, may be converted into gaseous fuel in the "generator" of Siemens' invention, and the advantages which attend the use of fuel in this form, apart from its employment in his furnaces, suggest a probably much wider field for its use in the future in connection with various branches of chemical manufacture. "Water-gas," essentially a mixture in various proportions of hydrogen, carbon monoxide, carbon dioxide, and atmospheric nitrogen, obtained by bringing water in contact with glowing carbon, whose combustion is properly regulated, seems to have first been distinctly noticed by Fontana in 1780, and has repeatedly since then attracted attention, but no arrangement for its ready production at will has combined so many practical advantages as the Siemens generator.

To some extent the immense natural supplies of combustible gas—chiefly methane and ethane—obtainable in portions of the petroleum region of Pennsylvania, Ohio and West Virginia, have been utilized as fuel, but the merely local character of such supply must always very much limit its importance.

The great loss of heat, amounting to about two-thirds of that producible from the fuel used, which is involved in allowing the formation in a furnace of carbon monoxide, and its escape unburnt or burned only to waste,* has come to be pretty generally understood; and especially from blast furnaces used in making pig-iron, is this gas now very commonly collected by means of suitable flues from the upper part of the furnace, and made use of not only for purposes connected with the working of the furnace itself, as raising steam for the engine and heating the blast, but occasionally as the means of producing heat for other objects, as burning lime, bricks, common pottery, &c. The time is not far back when this portion of the fuel was almost always wasted.

For certain purposes, though not most prominently for chemical manufactures, the use of *liquid* fuel claims serious attention; but the most valuable material of this kind which

*C burned to CO_2 evolves 96.960 heat units (obtained by complete combustion).
CO " " CO_2 " 67.284 " " (lost by escape of CO).

C escaping as CO " 29.676 " "

we possess, crude petroleum, distinguished by its great heat-producing power, its abundance and cheapness, still awaits a satisfactory solution of the problem of its application.

When lower temperatures than those directly resulting from combustion are required, steam becomes invaluable as the means of transmitting, distributing and regulating the supply of heat, and both at the boiling point and superheated, both at ordinary and high pressure, it plays a more and more important part in the arrangement of chemical factories, the water resulting from its condensation being at pleasure allowed to mingle with or excluded from the material heated, while the escape of steam itself is sometimes available as the means of producing mechanical agitation.

It may not be unworthy of mention that the "slag-wool" now produced upon a fairly large scale by blowing a jet of steam or air forcibly over the surface of furnace slag in a state of fusion, affords an excellent material for jacketting boilers, steam-pipes, hot-air flues, &c., in order to greatly diminish, by its low conducting power, the loss of heat in transmission, while danger from fire and annoyance from rotting or mouldering of organic substances, are obviated by the unalterable character of this mineral material.

Metallurgy — Iron.

The grand fact in the history of iron for the last twenty years has been the gradual but pretty rapid substitution of the softer varieties of steel to a very large extent for wrought iron. The earlier experiments of Bessemer and some others who worked at about the same time, were directed to the production of this latter material by a quicker and easier process than "puddling" for the removal of the carbon of cast-iron. These experiments were unsuccessful so far as the complete removal of carbon and production of thoroughly soft, pure iron was concerned; but they proved the feasibility of manufacturing steel directly from cast-iron with far less expenditure of time, fuel and labor than older methods, such as "cementation," involved, in which carbon had first to be removed, producing wrought iron, and subsequently added again slowly and in restricted amount. The new processes, moreover, carried with them the great advantage of operation at so high a temperature that the metal was completely fused, and hence much more uniform in character than when masses were consolidated by welding only from parts varying in the amount of carbon, and hence in physical properties, and retaining also in the case of bar-iron more or less remains of slag. It did not take long to show that these characteristically new processes were not destined to replace the older ones for the manufacture of wrought iron, properly so-called,

but it was not so quickly perceived that neither were they fitted for the production of the best steel, of such kinds as the name had previously been most connected with, and for such uses as it had previously been most largely applied to. Gradually it became apparent that the true function of the newly invented methods was mainly the production of a new material, containing carbon in relatively small amount, combining the toughness and workable qualities of wrought iron with the great tensile strength, rigidity, some of the hardness, and especially the homogeneity due to practicable fusibility, of steel. The "mild steel" which is the essential result of the recent processes of manufacture, is not the "tool steel" which not many years ago was pictured in every one's mind in connection with the name steel, but it is a substance available for a far wider range of uses and applicable upon a far greater scale.

Of the various individual processes which have been proposed and tried for the rapid production of mild steel, decidedly the most successful have been those of Bessemer and Siemens; the former consisting essentially in forcing a blast of air under high pressure into molten cast-iron in a suitable "converting vessel," thus rapidly burning out the carbon and silicon, mixing with the fluid metal a determined amount of separately fused cast-iron containing a known amount of carbon, and casting the product into ingot moulds; while the latter brings into play the admirable peculiarities of the gas furnace, by fusing together at the extremely high temperature which it affords, and in the entirely controllable chemical atmosphere of its hearth, pig-iron and scrap wrought-iron, as suggested by Martin, or pig-iron and iron ore (an oxide) on the plan of Uchatius, but on a much greater scale in either case, so apportioning the carbon and iron left together in the fused product that steel of the required character shall be obtained. In a sense it may be said that the invention of Siemens, leading to the manufacture of "Siemens-Martin" and "Landon-Siemens" steel, has supplemented the Bessemer converter, and by providing a way for profitably using up vast stores of old wrought-iron already on hand, has permitted the more rapid substitution of steel manufactured by both methods. By these two processes, within the last two or three years an annual product of more than 2,500,000 tons for the world at large has been turned out.

During the period in which so much attention has been concentrated upon steel, much has been learned in reference to the effect in its production and upon its properties of even very small quantities of other elements than iron, though much still remains to be ascertained in this direction.* The

*An important paper by V. Deshayes has recently been published (Bull. de la Soc. Chim. de Paris—20 Fév. & 5 Mars, 1879), giving the results of an extensive examination of the influence upon the physical properties of steel of its various minor constituents—phosphorus, silicon, manganese, &c.

most important points which have been ascertained are those in regard to the benefit derivable in the manufacture, particularly of Bessemer steel, from the presence in the iron of manganese and silicon; the chief function of the former being the removal, to some extent, of sulphur, phosphorus and oxygen, which, if allowed to remain, greatly impair the mechanical excellence of the product, while they exhibit a stronger tendency to combine with manganese than with iron, and thus get carried off into the slag; silicon, on the other hand, aiding by its combustion to keep up the high temperature in the converter which maintains the fluidity of the metal, and uniting when burned with the basic oxides to form and separate from the metal a removable form of fluid slag. The observed benefit arising from the presence of these two substances has stimulated the production, for use in connection with steel-making, of cast-iron rich in silicon, of crystalline "spiegel-eisen," containing a large and uniform amount of carbon along with manganese, and lately of alloys of iron and manganese—the so-called ferro-manganese—containing, as in the product of the French Terre-Noire works, up to 65, and even 85, per cent. of the latter metal. Another point, and of unexpected character, has but lately been ascertained—namely, that if the percentage of carbon in steel be reduced, phosphorus may be admitted to an extent which would be seriously injurious if the normal amount of carbon for the kind of steel required had been present. Some remarkable specimens of steel from works on the Siemens-Martin plan, in New Jersey, in the possession of the writer, illustrate this distinctly. Notwithstanding the numerous attempts, too often reported on by interested parties, to produce valuable alloyed forms of iron or steel by addition of other metals, most of which attempts have led to no permanent results of real importance, it remains much to be desired that a systematic examination should be made by impartial hands of the alloys of iron, with and without the presence of carbon, trustworthy analyses being made of the products, and at the same time their physical characters submitted to well-defined tests. Up to this time the only two of the more refractory metals which seem to have proved themselves capable of influencing in any useful way the properties of steel are tungsten and chromium, which give hardness, accompanied however by increased brittleness. The increase of retentive capacity for magnetism which tungsten is reported as producing may perhaps prove valuable in the construction of dynamo-electric machines.

As regards wrought-iron, whose day for many purposes can by no means be considered as gone by, the most notable manufacturing improvement has undoubtedly been the introduction of mechanical puddling as a substitute for the more laborious and less uniform hand-work. After many previous

attempts, success in this direction has come with the application of the rotating hearth, of which the Danks furnace arrangement deserves to be taken as the type. The more general use of currents of water through double furnace-walls as the means of allowing the highest temperatures within, with diminished risk of injury to the walls themselves, is an extension of the long-used water-backs of the refinery furnace.

For cast-iron, aside from the marked increase in the size of many of the furnaces built, and in some hands the use of a blast of considerably higher temperature than was usual a few years ago, the question of most interest has been that of the elimination from the metal of phosphorus and sulphur, particularly the former, with a view to the supply of metal to the steel-makers suited in this respect to their requirements, since the modern methods of steel manufacture do not tend to remove phosphorus if present, the Bessemer process even relatively increasing its amount, and its retention in the steel to any large extent being ordinarily in the highest degree objectionable. The comparative scarcity and therefore cost of ores originally free, or nearly so, from phosphorus, while others are abundant against which the presence of this element can alone be urged in objection, renders the problem one of great importance.* Of the many plans proposed for getting rid of the undesirable element, two seem most to deserve notice. It has been found that in Cleveland ironstone from Yorkshire in England, and the same is probably true of many other ores, the phosphorus exists mainly, if not solely, as calcium phosphate, and that by washing the ore with a solution of sulphurous acid, obtained by passing the sulphur dioxide from burning pyrites into water, a large proportion, up to even 90 per cent. of the phosphorus, may be dissolved out and removed. It has been urged against this process as a fatal objection that the ore must be in fine powder to allow sufficiently thorough contact with the liquid acid, while the pulverulent condition unfits it for smelting in the ordinary way. While this is true as regards after use in the blast furnace, it seems quite possible that ore in powder might be managed in the Siemens furnace for the production of "Landon" steel, and, in the absence of material naturally pure enough, this process of preparatory washing may yet find application to a certain extent. The other plan to be mentioned has more extensive claims to attention, if the facts upon which it rests are fully confirmed by further experience, and if it can be brought into practically workable shape. Mr. Lowthian Bell, to whose intelligently

* It seems possible that one of the main features of Heaton's process for making steel from cast-iron rich in phosphorus — viz. oxidation by sodium nitrate at the bottom of a converting vessel — may be revived in perhaps a more permanently successful form. M. Gruner asserts of late (Bull. de la Soc. d'Encourag. pour l'Indust. Nation. Jan. 1879) that phosphorus may be removed in either the Bessemer converter or the Siemens furnace if a refractory *basic* lining be substituted for one of siliceous material.

directed researches we owe much important information in regard to the chemistry of iron-smelting, believes he has ascertained that phosphorus may be in large measure removed from melted cast-iron by oxidation at a temperature lower than that suited for puddling, the oxygen being derived from a bath of molten oxide of iron or slag very rich in such oxide; though at a higher temperature, at all approaching that of the Bessemer converter, phosphorus would be taken up again by the iron from the very same slag. It is proposed that the iron shall be brought rapidly into contact with the rich slag by running it from the furnace into a circular converting vessel, revolving about its axis and containing the slag already in a state of fusion. In one experiment it was found that the phosphorus in iron from Cleveland ore could by such treatment be brought down to .055 per cent., while continued contact, at full puddling heat, with the puddling furnace slag which had served as the means of purification, raised the proportion of phosphorus again to .153 per cent. in 65 minutes, and to .365 per cent. in three hours. These experiments are suggestive and full of promise that a solution of this important problem will yet be found, though as yet it cannot be said to have been reached in a practically useful and generally applicable form.

In noting the chemical aspects of the iron and steel industry, as developed in the last quarter of a century, we can not overlook the magnificent scale upon which the mechanical appliances used in working the metal have outgrown their former dimensions.

A visit to such works as those of Creuzot in France, Krupp's establishment at Essen, in Germany, the heavy gun factories at Chatham and the armor-plate mills at Sheffield, in England, or even to several of the works which have grown up in this country, presents a truly impressive picture of mechanical power directed and controlled by human brains. Such a single tool as the great Creuzot steam-hammer, with its 75 or 80 tons of iron falling 18 feet upon an anvil of nearly 900 tons, and capable of forging masses of steel of 120 tons or more, represents a marvellous advance upon the means at the command of the iron-workers of fifty or even twenty years ago. Yet the very source of the demand for these mighty machine-tools, the growth of the manufacture of iron, and yet more steel, has in the improved character of the material produced opened up a still wider field and enlarged possibilities for the employment of mechanical energy upon the grandest scale.

(To be continued.)

NOTES.

Material for Standard Weights and Measures.

FRIED. MOHR suggests that a block of uncrystalline, black marble be used for the standard meter. The block should have the dimensions: 111 cm. in length; 20 cm. in height and breadth; *i. e.* it should be a parallelepipedon of 44,000 cc. The specific gravity being 2.7, the weight of the block would be 118.8 kilograms, or nearly 3½ cwt. These dimensions afford sufficient protection against, 1, breaking; 2, distortion; 3, sudden action of heat; 4, theft; and further they admit of the possibility of determining the temperature of the block exactly, as a thermometer can be sunk into a hole reaching to the middle of the block. The coefficient of expansion of black marble is 0.0000045 for 1° C. As the meter has 1000 mm., $\frac{1}{1000}$ mm. = 1 millionth part of a meter. 4.5 thousandths of a millimeter = $\frac{1}{222}$ mm., a distance which cannot be seen without the microscope.

The author considers rock-crystal the best material for weights, but as such weights would necessarily be very dear, he suggests the use of solid glass containing a large proportion of silicic acid. The conditions to be satisfied are: 1st. That all the weights should be made from materials of the same density; 2d. That the specific gravity of the pieces used should approach nearly to that of the substances commonly weighed; and 3d. That the weights should have a certain hardness to protect them from wear.—(*Annalen der Chemie*, 194, 1.)

Nitrous Oxide as an Anæsthetic Agent.

P. BERT has made some experiments on animals which indicate the possibility of employing nitrous oxide as an anæsthetic agent in the cases of operations requiring considerable time. The use of the gas is dangerous because it must be inhaled in pure condition, and hence suffocation soon follows in consequence of a lack of oxygen. The fact that the gas must be inhaled in pure condition signifies simply that its tension must be equal to one atmosphere in order that enough shall enter into the system. If, however, the patient is placed in an apparatus in which the pressure is increased to two atmospheres, then a mixture of 50 per cent. nitrous oxide and 50 per cent. air may be employed. The anæsthesia will be effected, while at the same time the normal quantity of oxygen

finds its way into the blood, and normal conditions of respiration are preserved. The author's experiments on animals showed the correctness of the above reasoning. Unconsciousness was reached while normal respiration continued, and this condition could be maintained for an hour. On removing the bag which contained the mixture of gases the animal returned to its normal condition after two or three inhalations of fresh air. During the action of the anæsthetic, the animal showed no signs of pain even when nerves laid bare for the purpose were subjected to pressure or when its limbs were amputated. No bad after-effects were observed.—(*Comptes rendus*, 87, 728.)

Purification of Mercury.

J. W. BRUEHL recommends the use of chromic acid for the purification of mercury. Twenty-five kilograms of mercury which contained a considerable quantity of Wood's metal were perfectly freed from the foreign substance in about two hours. To 1 liter water are added 5 gr. potassium bichromate and a few cubic centimetres sulphuric acid, and an equal volume of mercury is well shaken with this mixture. The metal breaks up into globules, while a very small quantity is transformed temporarily into red chromate. The flask is shaken until the red powder has disappeared, and the aqueous solution becomes pure green from the chromium sulphate formed. A strong current of water is now passed into the flask, and a fine gray powder which lies upon the surface of the mercury and between the globules, and consists of the oxides of the metals, is thus washed away. According to the degree of impurity this process is repeated once or twice more, and finally the whole is shaken with distilled water until no more gray powder is washed away, and the water remains perfectly clear.

This method was tested with a large quantity of waste mercury that had accumulated in the author's laboratory in consequence of the amalgamation of the zinc plates of a battery. Much of this mercury contained so much zinc, copper and lead that it was solid. In the course of an afternoon it was purified so completely that when shaken in a porcelain dish it did not leave a trace of a mark upon the porcelain.—(*Ber. deutsch. chem. Gesell.* XII. 205.)

On the Preparation of Hydrogen Sulphide in Chemico-Legal Examinations.

Formerly hydrogen sulphide for chemico-legal examinations was unhesitatingly prepared from crude materials, generally from commercial iron sulphide with crude sulphuric or hydrochloric acid, probably because it was thought that the formation of arsine in a liquid in which hydrogen sul-

phide is being evolved was impossible. In 1869 J. Otto found that arsine was contained in hydrogen sulphide from impure materials. Myers found later that arsine and hydrogen sulphide can exist in each other's presence at ordinary temperatures. Myers is of the opinion that the formation of arsine is due to the presence of arsenic in the acids and not in the iron sulphide. The author states that his own experiments serve in general to confirm the opinion of Myers, but he adds that the iron sulphide may also play a role in the formation of arsine.

Whatever the origin of the arsine may be, it is plain that hydrogen sulphide containing this impurity is not fit for use. *It is hence absolutely necessary to make the hydrogen sulphide used in forensic examinations from pure materials, free from arsenic.* Dragendorff recommends that the iron sulphide employed be made from washed flowers of sulphur and pure wrought iron, and that the first part of the distillate obtained in rectifying sulphuric acid be used for decomposing the sulphide. R. Otto recommends the use of calcium sulphide, which can be easily prepared by igniting gypsum with charcoal, and this he decomposes with pure hydrochloric acid. If the acid is allowed to drop slowly upon the calcium sulphide under water, the sulphide being broken up in coarse pieces, a quiet and regular current of pure hydrogen sulphide is obtained.—(*Ber. deutsch. ch. Gesell.* XII. 215.)

Notes on "Uranine."

The substance to which the trade name "Uranine" has been given is now to be found in the hands of dealers in coal tar dye-stuffs, and has of late been made the subject of various newspaper notices, drawing attention, sometimes in rather a fanciful way, to the remarkable fluorescence of its solution. The material appears as a red powder of somewhat the tint of cuprous oxide, directly soluble in water, the solution having an orange color by transmitted light, exhibiting vivid green fluorescence, and directly dyeing animal fabrics a bright golden yellow.

1. Qualitative examination shows that this coloring material is sodium-fluoresceine, readily developing by bromination the beautiful aurora red tints of eosine. Traces of the potassium and calcium compounds are also detectable by means of the spectroscope, but they are accidentally present only.

2. When the substance in the dry state is heated over a lamp flame, it undergoes partial fusion and rapid charring, producing a very voluminous coal, from the interior of which the fused and decomposing mass is rapidly pushed out in oddly contorted, worm-like cylinders, reproducing the appearance of the "Pharaoh's serpents" (of sulpho-cyanate of mercury) which were sold as toys a few years ago. This effect is most readily

observed with a little of the powder taken up on a loop at the end of a small platinum wire.

3. The fluorescence, which persists in extraordinarily dilute solutions, is not observable in those of more than a certain degree of concentration. In order to determine approximately what degree of dilution is needed to produce the phenomenon, 1 grm. of the powder was dissolved in 10 cc. of water at 15° C., and more water gradually added. With 40 cc. fluorescence began to be faintly seen; the effect was not well marked until about 100 cc. had been used, and it became notably more brilliant up to a dilution of about 1 : 2000.

This effect of dilution is suggestive of partial dissociation of the alkaline compound under the influence of the "mass" of the water, for on preparing a cold solution of a strength just too great to show fluorescence and applying heat, the green light became perceptible, while heating to an equal extent did not develop fluorescence if a lump of solid sodium hydrate had previously been dropped in and dissolved.

4. "Uranine" may be used as a distinctive test for bromine, the change from yellow to eosine-red being well marked, and the reaction producible with a small enough quantity to give it practical value. Thus, on dyeing a bit of white silk with a solution of 1 grm. uranine in 100 cc. of water and letting the fabric dry, .0005 grm. of bromine in (saturated) bromine water directly applied produced a minute rose-colored spot; .005 grm. of potassium bromide, representing .0033 grm. bromine, was placed in a very small test-tube with a few milligrammes each of manganese dioxide and sulphuric acid; a bit of white silk, 20 mm. by 4 mm., having a spot of 5 mm. by 2½ mm. dyed yellow with uranine, dried, and one half the surface of the spot slightly remoistened, was placed in the upper part of the tube, and the bottom was gently warmed, a fairly recognizable change from yellow to red of the moistened surface was produced. The change of color is not brought about by chlorine, iodine, or the lower oxides of nitrogen. Much chlorine along with bromine bleaches the fabric, but even then careful observation during the progress of the action will show the rosy tint around the edges of the spot which has been dyed.

Univ. of Va., Feb. 24, 1879. J. W. MALLETT.

The Amalgams of Chromium, Manganese, Iron, Cobalt and Nickel, and a new Process for the Preparation of Metallic Chromium.

H. MOISSAU states that when a concentrated solution of protochloride of chromium is shaken with sodium-amalgam, part of the latter decomposes water, and oxide of chromium is precipitated. Another part produces, by double decomposition, chloride of sodium and an amalgam of chromium. This freed

from sodium by boiling water is less liquid than mercury, becomes covered with a black layer of oxide on exposure to air, and is slowly decomposed in presence of dry air, more quickly in presence of water. Heated in hydrogen to 350° it leaves a residue of metallic chromium in the form of black, amorphous powder, which becomes suddenly incandescent when heated to red heat on platinum foil, and is converted into the green sesquioxide. The metallic chromium thus obtained is not attacked by boiling sulphuric acid nor by nitric acid, and only slowly by hot hydrochloric acid. This method of obtaining the amalgam is applicable to manganese, iron, cobalt and nickel. Schoenbein obtained in this way amalgams of iron and manganese, and Damour those of nickel and cobalt, by zinc amalgam. The author also obtained an amalgam of manganese by electrolysis of the protochloride, using a negative electrode of mercury. He was able in this way to obtain a crystallized product, which when distilled at 440° left manganese in the form of powder. This when touched with a drop of strong nitric acid became incandescent. It also decomposes water slowly at ordinary temperatures, more rapidly at 100°. Electrolysis also gave amalgams of nickel and cobalt, which were quite quickly oxidized by contact with water. The amalgams thus obtained were less rich than those of sodium, which fact the author attributes to opposing currents produced by the action of the amalgam upon the liquids in contact with it.—(*Comptes rendus*, 88, 180.)

Lead in Crystals of Potassium Iodide.

E. Schering calls attention to the fact that concentrated solutions of potassium iodide take up lead iodide. This is of special importance, inasmuch as the iodine employed in the manufacture of potassium iodide sometimes contains lead. In concentrated solutions of potassium iodide which contain lead, hydrogen sulphide at first causes a precipitate, but all the lead cannot be precipitated by this means; for the clear filtrate when further evaporated yields crystals containing lead. In order to remove all the lead from the potassium iodide it is necessary to dilute the solution greatly, and then precipitate by means of hydrogen sulphide.—(*Ber. deutsch. chem. Gesell.* XII. 156.)

Photographic Observations of the Spectrum of Oxygen.

Hermann W. Vogel has photographed the spectrum of pure oxygen, using for the purpose the gelatine bromide of silver plates prepared by Wratten and Wainwright in England. These plates, which have only recently been introduced, are *fifteen times* more sensitive than the most sensitive known wet

plates. The photographs will be published in the "Berichte der kgl. Akademie der Wissenschaften in Berlin."

The photograph of the spectrum of *hydrogen* (obtained by electrolysis and by heating potassium formate) has also been taken successfully. In this, not only the three known lines in the blue and violet are shown excellently, but also the red line *Ha*, coincident with the *C* line of the sun, and a number of other lines, of which some belong to mercury, and others still remain to be determined. The author further states, that the fourth hydrogen line (coincident with "*h*" of the sun) could always be observed by Paalzow and himself with the naked eye, using the simple induction current, notwithstanding the assertion of Lockyer, that this line is visible only at a very high temperature, such as is produced by interposing a Leyden jar.

The photographic observation of the spectra of the most important gases will be continued by the author together with Paalzow.—(*Ber. deutsch. chem. Gesell.* XII. 332.)

A New Chemical Industry established by M. Camille Vincent.

In countries where sugar is made from the beet the molasses has for a long time been employed to yield alcohol by fermentation. The juice of the beet, as well as that of the sugar-cane, contains, in addition to the sugar, a large quantity of extractive and nitrogenous matters, together with considerable quantities of alkaline salts. The waste liquids or spent-wash from the still—called *vinasses* in French—are wastefully and ignorantly thrown away instead of being returned to the land as a fertilizer.

In France where the liquids (*vinasses*) are evaporated to dryness and calcined in order to save the alkaline salts, it is now shown by M. Vincent that the volatile matter given off in the process of calcination may be utilized. Among the products obtained is trimethylamine. When the hydrochloric acid salt of this base in heated to 260° it yields ammonia, free trimethylamine and chloride of methyl:

$$3N(CH_3)_3HCl = 2N(CH_3)_3 + NH_3 + 3CH_3Cl.$$

Large quantities of methyl chloride are thus produced, and this can be used in producing cold, and in preparing certain methylated dyes. Thus a new branch of chemical industry is opened. The subject will be treated more fully in a later number of this journal.—(*Nature*, Vol. 19, p. 308; and *Dingler's polytect. Journal*, Vol. 230.)

Kolbe's Criticism of Baeyer's Address.

Last year Baeyer gave an address before the Royal Academy of Sciences at Munich, which Kolbe has recently made the subject of a scathing criticism of a novel character. After a

few introductory remarks of a decidedly uncomplimentary nature, and quite characteristic of the writer, he reprints in his own journal* Baeyer's address in full in very heavy type, adding here and there a sharp footnote, or an expressive word or two in parenthesis. The address is called a dream because, according to Kolbe, it could not have been the result of thought.

Much of the criticism is expressed by means of interrogation and exclamation points, employed either separately or together; while the words "nonsense," "phrase," "style," "logic," are employed extensively in order to call the reader's attention to the particular kind of error which the writer of the address has committed. We quote some of the longer footnotes in order to give a fairer idea of the criticism. At the beginning of his address Baeyer alludes to Wœhler's discovery of the artificial formation of urea and uses the words, "Considered by itself (it is) only of secondary interest." To this Kolbe remarks: "Wœhler's discovery . . . was considered from the beginning, and is still considered to be one of the most important discoveries which have been made in this century in the department lying between organic and inorganic chemistry, and not only, as Baeyer says, because it formed an epoch in the history of human knowledge, but also because the change which takes place in the transformation of ammonium cyanate into urea by a rearrangement of the atoms in the molecule of the former, *considered by itself* is of the greatest interest even at the present day, when the opinions of chemists in regard to the nature of this change still differ widely." "It is impossible to see what Baeyer had in mind when he wrote the passage and what standard he employs when he characterizes Wœhler's discovery of the artificial formation of urea as one which, considered by itself, is only of secondary importance." Again when Baeyer says, "Wœhler's discovery appearing in the most modest garb," Kolbe remarks: "The modesty of the German chemists in the classical period of chemistry, to-day arrests attention and occasions surprise—a characteristic of the present."

In referring to Baeyer's discussion in regard to the size of molecules and their number in a given space, the critic says: "Nothing is simpler, and at the same time more thankless and worthless, than to make such calculations, in which particularly para-physicists take pleasure. In contradistinction to the real, experimenting physicists, the *ortho-physicists*, who by further experiments test the conclusions which they draw from their experimental investigations, I call those *para-physicists* who by preference use the experimental investigations of others for the purpose of setting up hypotheses, but neglect to test their hypotheses by means of their own, new experiments. It is again particularly the modern chemists who are impressed

* Journal für prak. Ch. N. F. 18, 432.

by these hypotheses. The third class of physicists, the *metaphysicists*, believe that they can entirely dispense with the experimental foundation in their phantasies in natural philosophy."

The article, with all its curious additions, is certainly interesting and instructive reading.

Monument to Liebig.

The last report of the committee of German chemists on the Liebig monument was given by Hofmann at the last general meeting of the German Chemical Society. A prize was first offered for models, the competition being open to artists of all nations. About twenty models were sent in. These were exhibited in Berlin for three weeks and then sent to Munich, where they were again placed on exhibition. A jury consisting of well-known chemists from different countries, and of artists and other persons of acknowledged critical ability, passed judgment upon the models exhibited, and after considering the matter for two days, awarded the first prize to Professor Mich. Wagmueller of Munich. The Monument Committee then decided to enter into negotiations with Prof. Wagmueller, and obtained from him an estimate of the cost of the monument. The estimate was 107,000 marks ($26,000). It was finally decided by a vote of 3 to 2 to have the statue for Munich made of marble, and that for Giessen of bronze. Professor Hofmann was opposed to the use of marble, and in his remarks before the German Chemical Society he said: "I must confess that my feelings of objection to the erection of a marble statue in Munich are not fully removed; at the same time, the erection of the same statue in marble and in bronze under nearly the same conditions as regards climate, may be regarded as an interesting experiment, the results of which may furnish the chemists of the next century with important points for a decision of the disputed question, *bronze* vs. *marble*."

Death of Heinrich Geissler.

A loss which all chemists feel is occasioned by the death of Heinrich Geissler of Bonn. In a quiet way this man has done a great deal to advance the physical sciences by devising and perfecting many pieces of glass apparatus in daily use in laboratories. His skill in delicate glass-blowing is too well known to require a word of notice here. His name is perhaps most frequently connected with the so-called Geissler tubes for studying different kinds of electric discharge in rarefied gases or vapors. Besides his well-known mechanical labors, Geissler was engaged in some investigations of a purely scientific character, particularly such as depended for their success upon the construction of peculiarly delicate pieces of apparatus. He died on the 24th of January, at Bonn.

NEW PUBLICATIONS RELATING TO CHEMISTRY.

I.—American.

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P. 40, line 9 from bottom, *insert* "were performed" between "experiments" and "for."
P. 53, line 23 from top, *insert* "of" between "formula" and "benzol."
P. 54. The left-hand diagram at bottom should have only one short line projecting from each angle.